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GEORGE REID
Editor

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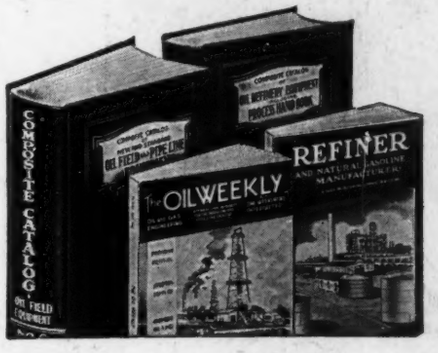

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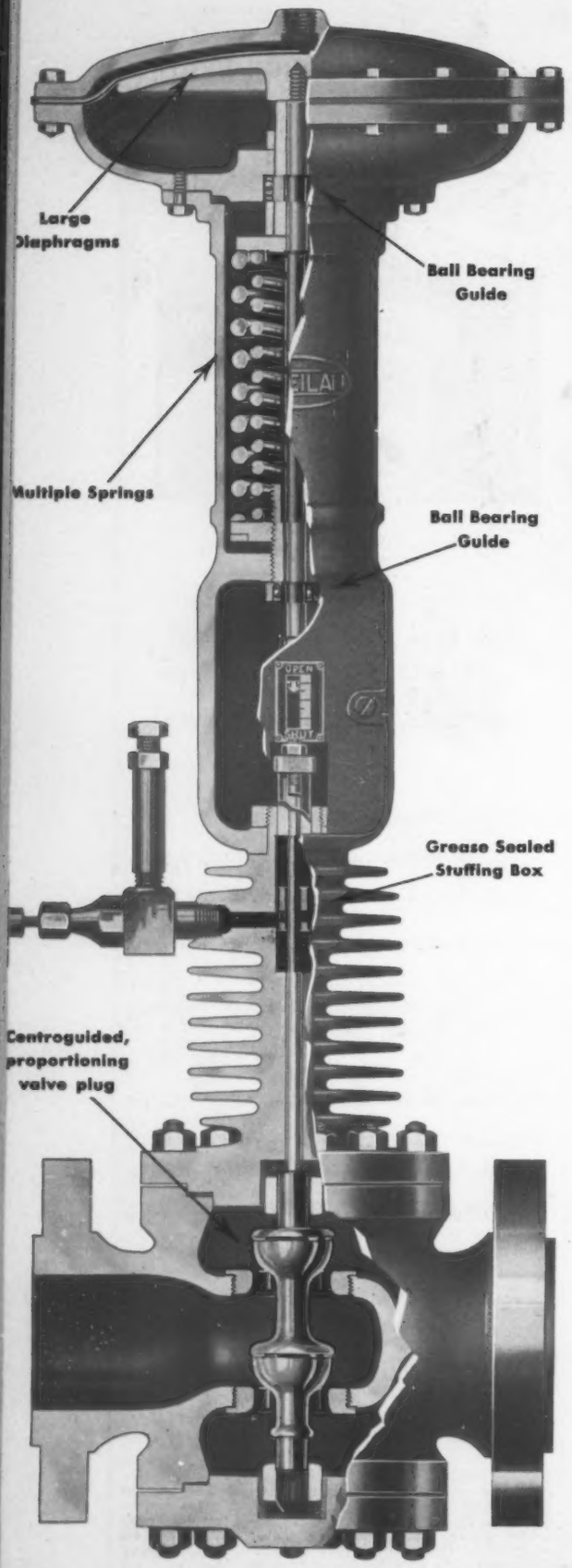

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CONTROL IS ONLY AS GOOD AS ITS VALVE

Catalytic Polymerization and Copper Sweetening

Sunray Installation

J. C. ALBRIGHT

JANUARY 26, 1939, Sunray Oil Company, Allen, Oklahoma, had operated its recently complete U.O.P. catalytic polymerization plant for 32 days. Within a few hours after circulation had been established the meter on the liquid line from the polymerization plant stabilizer had registered the first gallon of production, and the plant has continued to operate with an efficiency indicating around 95 percent conversion of olefins. The plant has been remarkably free of operating difficulties, and it has not been necessary to shut off the flow to make adjustments.

The catalytic polymerization unit is designed to process up to 800,000 cubic feet of gas daily as a peak load, using about 400,000 cubic feet of fresh gas from the pressure-distillate stabilizer and a like amount of recycle gas from the overhead discard of the polymerization-stabilizer column. The recycle is said to reduce the tendency of the catalyst to over polymerize and form an extremely heavy product with a high end point. The use of recycle makes it possible for catalyst towers to be constructed sufficiently large, that, when the catalyst begins to deteriorate, the recycle gas may be gradually reduced so the rich gas may contact a greater surface, in relation to the gas input, to obtain adequate reaction and maintain the initial high percentage of olefin conversion.

The refinery at Allen may be adjusted to produce a variable amount of gas originating in the cracking unit by varying the operation of the pressure-distillate stabilizer, and in the same way increase or decrease the amount of olefins in the gas. The deeper the pressure distillate is stabilized, the greater the percentage of unsaturates in the gas, and with the cracking plant running 3600 barrels of oil per day, the volume of gas available for processing through the catalytic polymerization plant is about 550,000 cubic feet. The amount which would represent the most efficient operation for the pressure-distillate stabilizer and the catalytic polymerization plant is that recovered from pressure-distillate stabilizer overhead when the pressure distillate is reduced not lower than 5 pounds Reid vapor pressure. At this vapor pressure, the 550,000 cubic feet of gas would contain 35 percent olefins.

If the pressure-distillate stabilizer were operated under a set of conditions which would produce a product of 11 pounds Reid vapor pressure, the amount of gas leaving the reflux condenser would be about 400,000 cubic feet, containing about 30 percent of available olefins. Therefore, the production of catalytic polymer gasoline depends upon the operation of the pressure-distillate stabilizer, primarily, where the raw gas is provided for the catalytic plant.

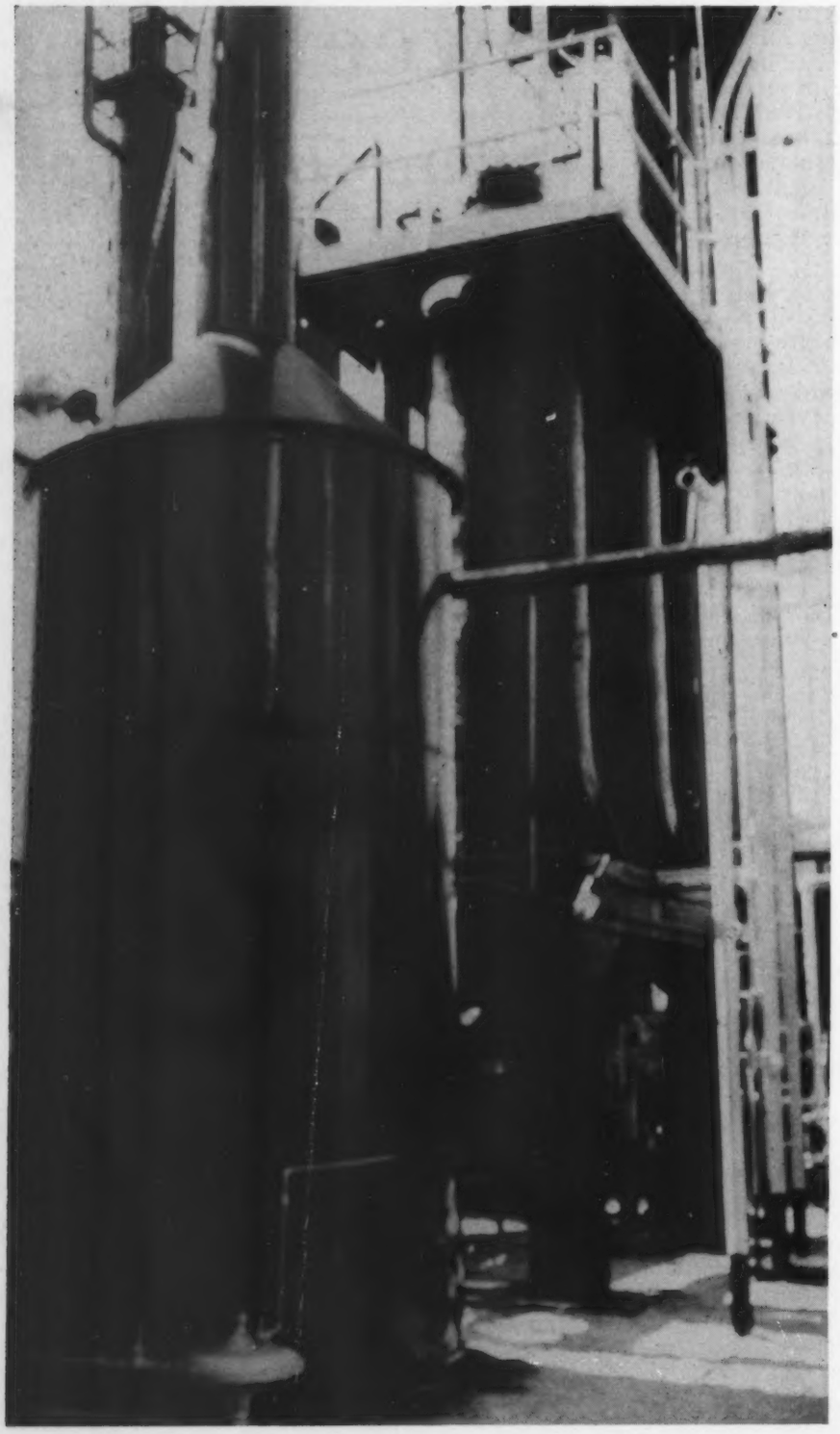
The polymerization plant contains two catalytic towers designed for operation in series, each of which is filled with 3150 pounds of Universal Oil Products Company, 3/16-inch catalyst; a gas-engine-driven compressor to obtain the required pressure for operating the conversion plant; a heater to obtain the necessary temperature; a water injection pump; heat exchangers; condensers and a final polymer stabilizer with an overhead reflux condenser. The gas engine is rated at 50 horsepower and is a four-cycle, single-cylinder horizontal unit with a common crankshaft for both the power and compressor cylinder connecting rods. The engine has an adjustable volumetric controller, operated with a large handwheel so the operators may compensate for the volume of gas handled.

All of the gas is handled by this compressor and is discharged to the gas heater outside the compressor building. The suction of the compressor is connected to the piping carrying the gas supply, where the volume of recycle gas is controlled as it is admitted to the suction of the compressor along with the raw stabilizer gas from the pressure distillate reduction column. The suction piping is made up as a manifold with automatic valves which release excess recycle gas from the polymer stabilizer to the plant gas lines to be used as fuel or returned to the plant absorption system to recover any fractions not converted, or the butanes which may have been fractionated out of the pressure distillate when cutting to a very low vapor pressure product. A steam heated pot is inserted in the suction manifold to vaporize any liquid entrained with the rich gas, to prevent condensate from reaching the gas compressor cylinder.

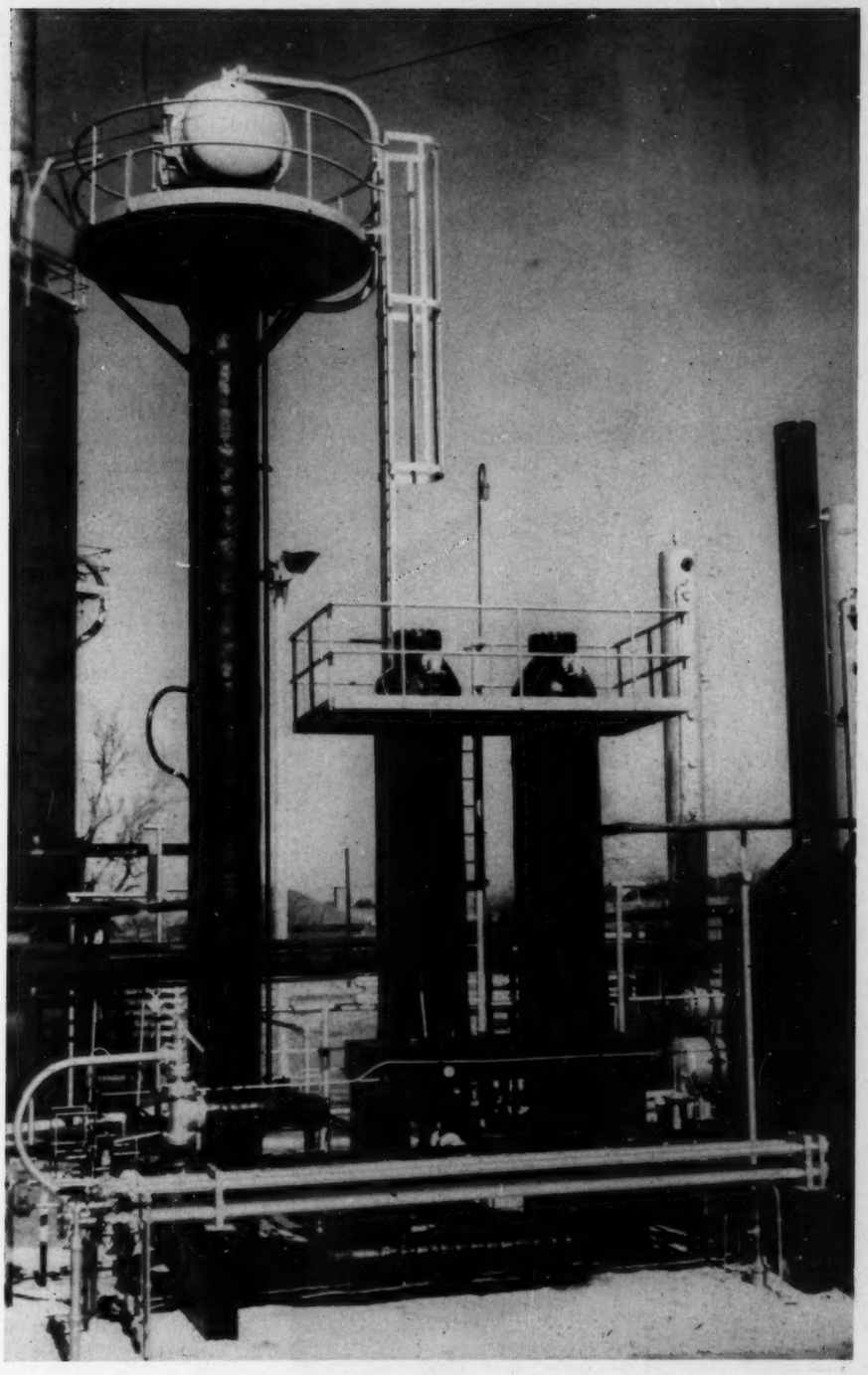
A 3-inch discharge line connects the gas compressor cylinder to the gas heater, with connections attached to this pipe where water is introduced for the control of hydration of the catalyst. A 1¼-inch by 2½-inch relief valve is inserted between the compressor and the inlet of the heater element to remove gas from the system when excessive pressures are encountered and as a protective measure for the plant. The water injection is controlled with a small pump, similar in design to an engine lubri-

cator, driven by an electric motor and with adjustable feed so that as little as 4 cubic centimeters of water may be injected into the gas per hour. The water pump is made with two feed pistons, one connected to the 3-inch piping before the gas reaches the heater, and the other to the piping between the two catalyst towers.

The heater in this polymerization plant is a cylindrical furnace containing a helix made of 2-inch, 600-pound test, seamless pipe containing 200 square feet of heating surface. A stack is connected to the upper section containing a damper to control the draft through the furnace. It is fired with a single burner at the base with gas admitted through a valve actuated by a recording thermometer control instrument. The flow of gas through the heater piping is from top to base, countercurrent to the passage of heat from the gas burner to the furnace stack. Fuel for this furnace is obtained from the refinery gas system, which is extended to the gas engine for fuel for this unit. The gas from the heater has a normal transfer temperature of 385° F. and passes to the first catalyst column under a pressure of 485 pounds, gauge.



Heater used in catalytic polymerization plant, with catalysts columns in the background.



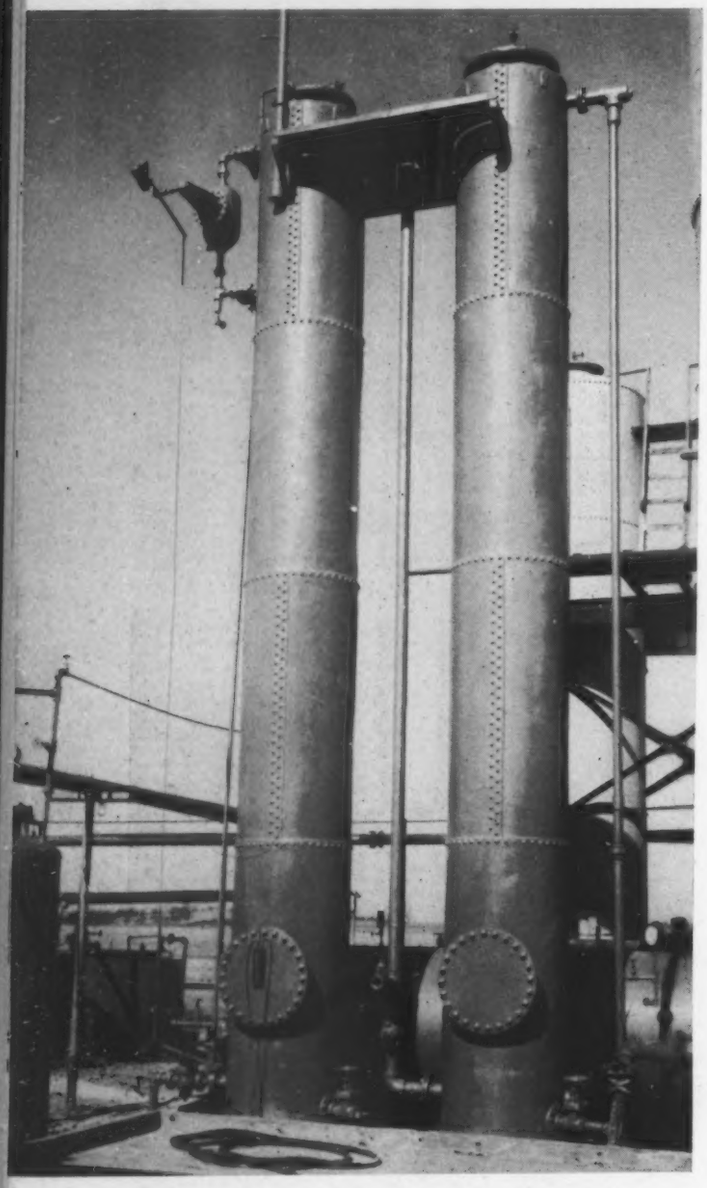
Catalytic polymerization system, with catalytic towers in center and stabilizer at left.

The catalyst towers are installed in a vertical position upon steel and concrete structures which bring the base of the columns sufficiently high above the ground level for convenience in removing the catalyst when this operation is required. The columns themselves have a diameter of 2 feet 6 inches, and a height of 15 feet 6 inches. Each end is swedged down from the cylinder size; the top to 12 inches, and the base to 16 inches. Both ends are closed with bolted man-hole covers, the top a blind flange and the lower equipped with a 3-inch pipe nipple for gas exit. Each tower is equipped with a steel supporting screen near the lower flanged outlet, upon which is placed two layers of crushed fire brick. The lowest is graded as coarse, and the upper layer as fines. This supports the bed of catalyst which is placed in the towers in an unbroken bed to reach the top gas connection. The walls of the towers are 15/16-inch thick and the outer surface is covered with insulation having a thickness of 2 inches.

The flow of gas through the catalytic polymerization plant is in series, entering the towers at the top and leaving at the base. The temperature of the gas as it leaves the first tower is 450° F., having been increased from 385° F. by the exothermic reaction between the catalyst and the olefins in the gas charge. Between 4½ and 5 cubic centimeters of water per hour are injected in the transfer line between the two catalyst towers to control the hydration of the catalyst in the second column. The outlet temperature of the gas from the second tower is about 460° F. but is never permitted to exceed 480° F.

The polymer gasoline is condensed in two sectional water-cooled units, and the liquid and vapor pass

to the stabilizer. This column is constructed of 24-inch O.D. pipe having a wall thickness of ½-inch and is 30 feet 6 inches high, equipped with a shell-and-tube reflux condenser mounted above the top gas outlet flange, with a 12-inch pipe connection between the stabilizer and the shell of the reflux condenser. A perforated plate placed about 36 inches above the



Treating columns in copper treating plant. Secondary treater at left is equipped with liquid level control at top which operates valve at the base to maintain conditions for expulsion of air.

base of the stabilizer supports 25 feet of ½-inch raschig-ring packing, which is used instead of the conventional bubble trays as the efficiency is adequate for this purpose and the cost is considerably less. The nozzle to admit the charge of liquids and gases to the stabilizer is installed at about the mid-section, which causes the lower part to act as a stripper for the liquids, and the upper section to act as a fractionator for the vapors in the same fashion that a bubble-plate tower functions.

The fractionator is equipped with a shell-and-tube, steam-heated reboiler which is operated at a temperature of 270° F., and the top of the column is controlled by water flowing through the tubes of the reflux condenser, adjusted to obtain the desired vapor pressure product in the base of the stabilizer. The column is operated at a pressure of 245 pounds, gauge, controlled with an automatic instrument installed in the 1½-inch dry gas line from the stabilizer top. The pressure on the column is obtained by a reduction of process pressure at the outlet of the polymer condenser, therefore no intercompressors or pumps are required for stabilizer operation.

The results obtained with this polymer plant has been of the order of 95 percent conversion of olefins. The combined feed to the plant, a mixture of about 50 percent raw stabilizer gas and 50 percent polymer stabilizer overhead discard, contains an average of about 20 percent available olefins. The amount of production of the plant depends upon what vapor pressure is desired on the stabilized polymer, but averages about 3500 gallons per day, when the pressure distillate is stabilized to 5 pounds, Reid vapor pressure, assuming that the cracking plant produces 550,000 cubic feet of gas which has an olefin content of 35 percent.

Facilities are provided in the system to transfer the stabilized polymer gasoline from the stabilizer to storage, or to any point desired in the refinery without pumping. The liquid is released from the base of the column through the action of an internal float remotely controlling a balanced valve in the transfer line to maintain the required level in the stabilizer. The liquid resulting from stabilization of the polymer gasoline is cooled in two horizontal sections with water used to reduce the temperature to that required for handling. A mechanical meter is installed in the 1-inch polymer gasoline to storage line to indicate and register the number of gallons produced. At the time the plant had been operated 32 days, the polymer gasoline was passed from the stabilizer to a copper treating plant for finishing and blending with other refinery products, together with an inhibitor to prevent the formation of gums.

The grade of polymer gasoline produced at that time was as follows:

A.P.I. Gravity	73° F.
Initial boiling point	62° F.
10 percent over	118° F.
50 percent over	240° F.
81 percent over	426° F.
End point	426° F.
Vapor pressure	24 lbs. Reid
A.S.T.M. Gum	.7 mgs.
Copper dish gum—After inhibitor	1.0 mgs.
Blending value for cracked gasoline	95
Blending value for straight-run gasoline	110/120
Color	blue

The polymer plant is designed as a non-regenerative unit, with the expectation of obtaining the full value of the catalyst over a period of time, and dumping the columns and recharging when the catalyst falls below a predetermined efficiency. This period may vary, depending upon economics which affects operating conditions, and the price of the finished products indicates whether to continue with a low percentage of conversion, or purchase new catalyst.

COPPER TREATING

Following completion of the polymerization unit a copper treating system was installed in which either straight polymer gasoline or a blend of cracked and polymer gasoline may be treated to produce a doctor-sweet and non-corrosive product. Two towers, 30 inches by 19 feet in size, to contain the chemical re-

agents, are used in the copper treating system. Since the gasoline contains hydrogen sulfide, a third vessel is used for a caustic-washing operation, and a fourth vessel, filled with sand, is employed to remove traces of moisture and to prevent carry-over of caustic into the copper treating system.

Any grade or blend of gasoline may be treated in this plant, which has a capacity of 2100 barrels per day, but materials may be passed through it at a rate of less than 100 barrels per day, as, for example, when treating unblended polymer gasoline as it comes directly off the stabilizer. Only one pump is installed in the treating plant, and that used to circulate caustic from the wash tank through a mixer as the gasoline enters this drum.

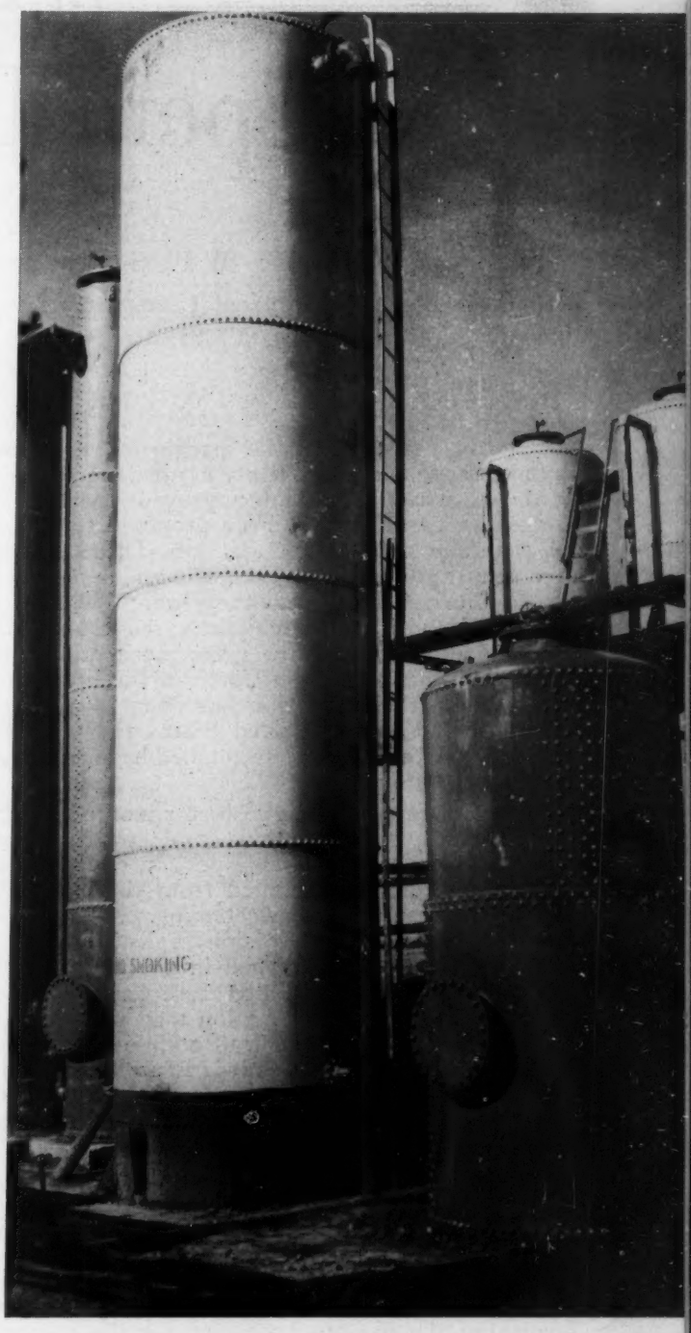
The two columns are identical, so far as outside appearance is concerned, but differ slightly in internal construction, due to the difference in the chemicals used and their function. The first column has a supporting tray near the base, and below the lower manhole, to support the bed of treating reagent. The upper end contains a spray plate to distribute the product being treated uniformly over the top of the reagent to prevent channeling. The second column has a supporting plate inside at the same distance from the base as that in the first column, upon which is placed a charge of a second reagent. The first column contains 2500 pounds of reagent, and the second column 4000 pounds. The top of the second column is fitted internally with a vertical baffle across the center, and placed so the incoming fluid will be forced through with a certain degree of turbulence. A liquid-lever controller, installed on piping outside the column near the top rontrols the level of gasoline in this tower by direct connection with a fluid valve in the outlet line attached to the base of the column.

When treating any product, the liquid enters the precaustic wash tank at one end (the vessel lies horizontally) where the caustic solution and the material being treated are intimately mixed. Caustic is recycled, but the product flows through the vessel and leaves at the opposite end at the top of the shell. A vertical tank, filled with sand receives the product as it enters near the top head, to pass down through the sand filter bed to be removed near the base. The product receives a predetermined amount of air between the outlet of the sand filter and inlet of the first treating column. Air and gasoline flow through the bed of reagent and are taken off at the base through a line connected to the top of the second treating column.

As the gasoline and air strike the vertical baffle, the turbulence created by the change in direction of flow is sufficient to separate the air from the liquid. A small pipe line from the off-center side opposite the gasoline inlet connection at the top removes the air which is piped outside the treating area and vented. The level is maintained at sufficient height in the second tower to provide adequate turbulence in flow to separate air, by the use of the outside liquid-level controller. As the gas leaves the base of the second column, it may or may not be treated additionally, but the usual procedure is to mix the required amount of inhibitor before the material enters storage tanks.

Two small drums are installed near the second treating column to contain the liquid inhibitor. These are equipped with the necessary controls to admit the required volume constantly through a mixing valve just outside the liquid-level-control valve. This line is connected to the refinery distribution system in order that finished gasoline leaving the treating plant may be placed in proper storage.

Since the polymerization plant is operated at sufficient pressure to process the gasoline in the final stabilizer, the pressure after the material passes through the mechanical meter is sufficient to treat



Caustic wash tower for removal of hydrogen sulfide, with sand settler vessel, right foreground, for removal of moisture and traces of caustic prior to treating in copper system.

in the copper sweetener without pumping. If a blend of cracked gasoline with polymer gasoline is treated, this mixture must be pumped from storage, likewise a blend of straight-run and polymer gasoline must be handled in a similar manner.

The product, regardless of its percentage of polymer gasoline, after treating shows negative to both doctor and corrosion test.

Effect of Hydrogen Peroxide *In Regeneration of* Spent Doctor Solutions

VIRDEN W. WILSON
Buffalo Electro-Chemical Company, Inc.
Buffalo, N. Y.

IN recent years, when the margin of profit in refining have been practically non-existent or cut to the bone, many new and improved processes for sweetening gasoline have been proposed to supplant the generally used doctor solution. These processes have been in many cases excellent under the operating conditions for which they were devised, and savings of considerable magnitude have been made by their adoption. Whatever the merit of the processes which have been put forth in the literature in recent years, their adoption has been by no means universal, and in the United States today, at least 85 percent of the gasoline sweetened has been treated by the plumbite process.

Cost of sweetening by the doctor method has been cut materially by adoption of doctor-reclamation units, wherein a considerable portion of the litharge used in treating is reclaimed from the lead sulfide formed in the plumbite sweetening reaction. Doctor reclamation, or the conversion of lead sulfide into litharge, can be accomplished in a variety of ways. A glance at the patent literature relating to this subject reveals that reclamation may be done either in liquid phase, with the lead sulfide suspended in the caustic medium, just as it is withdrawn from the separators in the treating system, or in a solid or semi-solid phase obtained by separating the blackstrap from the residual caustic.

Most refiners, however, have been content to install a small batch or continuous reclamation unit, usually a tank or tower, equipped with some means of heating the spent doctor solution, a swing line for the separation of such gasoline as may be withdrawn with the spent treating solution, and an air line for furnishing the oxygen necessary for the conversion reaction.

A quantity of spent treating solution is withdrawn from the treating system and charged to the reclamation unit, after which the material is heated gently to 120-150° F. If the blackstrap contains considerable quantities of gasoline in a tightly held emulsion, it may be necessary to heat the solution somewhat hotter in order to break this emulsion and release the gasoline, which can then be drawn off through the swing line. A gentle stream of air is directed through the solution, and heating is continued until the material has reached a temperature of 170-200° F. The air stream is then increased, and the doctor solution maintained at about this temperature throughout the course of the reclamation reaction.

After several hours blowing, samples are taken and checked for the soluble lead content, and when the solution approaches clarification, the steam coils are shut down, the air stream is cut off, the reclaimed doctor solution is withdrawn from the reclamation unit to storage, and additional litharge is added to bring the lead content of the solution to the desired level before further use is made of the treating solution.

The reaction consumes some caustic soda, which must be added from time to time to keep up the caustic strength of the solution, and the sulfur associated with the lead sulfide in the spent solution forms thiosulfates, and at times sulfates, which accumulate as the sodium salt in the doctor solution. It is customary when adding fresh caustic to withdraw and discard a small portion of the lead-free caustic solution to keep the thio-sulfate content below 7-8 pounds $Na_2S_2O_3$ per barrel.

The reclamation process described above has been shown to cut the cost of doctor sweetening appreciably, without necessitating undue investment in equipment, or excessive labor of operation.

In a series of investigations on the improvement of present doctor reclamation processes, it has been found that the addition of a small quantity of concentrated hydrogen peroxide together with air at the outset of the normal air reclamation would improve greatly the reclamation characteristics of the doctor solution. The introduction of the hydrogen peroxide may be accomplished in a variety of ways but it is important that the peroxide be added uniformly and contacted with as much of the spent solution as possible. The quantity of hydrogen peroxide to be added varies with the characteristics of the spent doctor; it appears to be an empirical function related to the total quantity of lead (either oxide or sulfide) present in the spent doctor, the age of the doctor solution (and consequently the non-reactive solids content) and the desired soluble lead content of the reclaimed plumbite solution. The results obtained by the use of hydrogen peroxide are such as to justify economically the application of this oxidizing agent as a promoter for the reclamation reaction. The process has in the meantime, been demonstrated to have excellent economic value.

The mechanism of the promoter reaction of hydrogen peroxide is believed to be two fold: first, there is undoubtedly some reaction directly between the nascent oxygen released on decomposition of the

peroxide, and the lead sulfide of the spent doctor solution; second, there is a promoter or catalytic reaction in which the hydrogen peroxide acts upon some other substance present in the spent doctor, in such a way as to "activate the solution" so that subsequent air blowing results in rapid, clean conversion of the lead sulfide to soluble litharge.

One explanation which seems in accord with the experimental evidence is that the lead sulfide in spent doctor used for sweetening cracked gasoline is covered with a very tightly adsorbed film of unsaturates, probably those containing conjugated double bonds. This adsorbed film may be extracted with benzol and some rough idea of the amount thus dissolved can be obtained by evaporation of this benzol extract in a glass dish. The hydrogen peroxide, when added in a fairly concentrated form, is a powerful oxidizing agent which reacts partially with these adsorbed unsaturates in the presence of lead sulfide to form soluble soaps which are dissolved in the caustic. The clean surface of the lead sulfide is then readied for reaction with the molecular oxygen provided by the air passing through the solution.

It is also well known that the lower-molecular-weight mercaptans present in sour gasolines will form insoluble lead salts which greatly retard the action of air in the regeneration of spent doctor solutions. It has been found that hydrogen peroxide is preferentially reactive toward these lead mercaptides, destroying them immediately with the formation of lead oxide and the release of the organic disulfide. While it is true that the common practice of caustic washing before treating gasoline has reduced this hazard appreciably, it has been found that in many cases a slight cloudiness of the caustic- washed gasoline indicates a carryover of sodium mercaptides which resulted in appreciable loss in the efficiency of the reclamation unit. The use of hydrogen peroxide in connection with the reclamation of spent doctor solution from one such unit resulted in an immediate increase in the reclamation unit efficiency.

The comparative reclamation performances with and without hydrogen peroxide over a period of time are given herewith in order that an evaluation of the process may be made. It must be borne in mind that no two reclamations behave in exactly the same manner, and that it is more important to give heed to the difference between reclamations with and without hydrogen peroxide. In other words, the absolute values for litharge contents and their rates of formation are of less interest than the comparative contents and rates of formation based on the two methods of operation.

The data given in Tables 1 and 2 are those obtained on full-size-plant tests made with and without hydrogen peroxide. Table 3 is included in order that the reader may be familiar with the particular type of doctor solution on which this reclamation comparison was made.

The data given in Tables 1 and 2 represent soluble lead contents (calculated as PbO) of various doctor

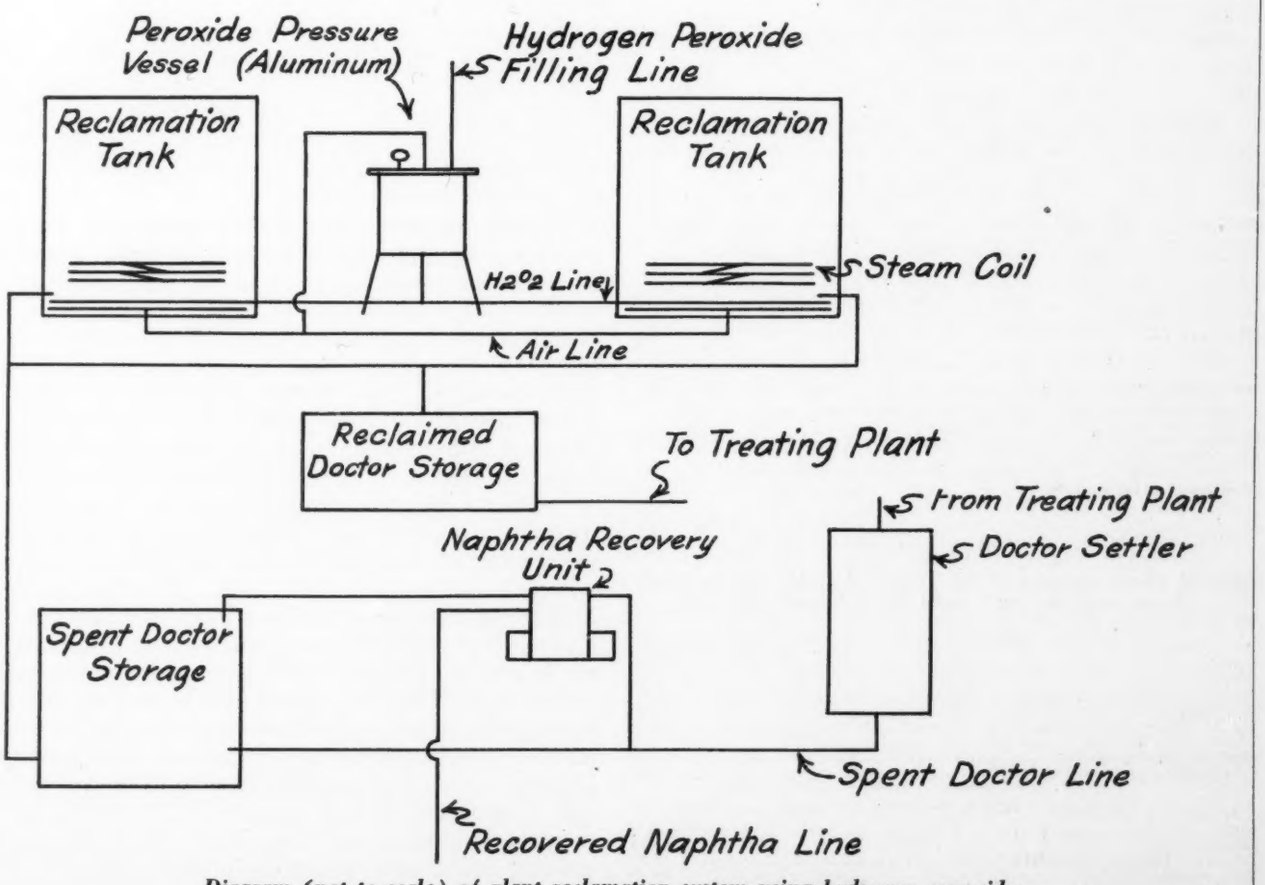


Diagram (not to scale) of plant reclamation system using hydrogen peroxide.

solutions treated with air alone and with hydrogen peroxide and air. These data were obtained from batch reclamations in which 230-250 barrels of partially spent doctor were regenerated at temperatures of 160-180° F. Since the reclamations were made to clarification of the solution and no lead sulfide was allowed to go back into the treating system, it was found that temperatures of 190-200° F. had no injurious effect on the quality of the reclaimed doctor solution, although no advantage was secured in going above 170° F. in the cases where hydrogen peroxide was added to the spent solution.

The reclamations were made (in the case of the air regenerations reported in Table 1) under normal conditions of operation, and the hydrogen peroxide-air regenerations (reported in Table 2) were made alternately with a number of air reclamations in order to rule out, so far as possible, non-comparable conditions.

TABLE 1

Air Reclamations at 160-180° F.

RUN No.	LITHARGE CONTENT Pounds PbO/Gallon Doctor Solution					
	Original	½ Hour	1 Hour	2 Hours	3 Hours	Final
1	0.050	0.062	0.071	0.071	0.075	0.093
2	0.050	.....	0.093	0.093	0.098	0.098
3	0.086	0.093	0.093	0.100	0.106	0.106
4	0.083	0.089	0.089	0.094	0.094	0.094
6	0.047	0.054	0.060	0.069	0.077	0.077
8	0.071	0.079	0.080	0.087	0.089	0.089
9	0.036	.....	0.054	0.059	0.060	0.060
10	0.042	0.048	0.060	0.060	0.060	0.060
11	0.048	0.054	0.060	0.072	0.078	0.084
12	0.042	0.048	0.060	0.072	0.078	0.078
13	0.044	0.047	0.053	0.070	0.078	0.078
15	0.043	0.049	0.054	0.060	0.066	0.070
Average	0.0535	0.0623	0.0690	0.0772	0.0794	0.0823

Average charge to reclamation tank: 9,880 gallons.
Average time of reclamation: 4½ hours.
Time in hours refer to period of blowing with air at reclamation temperature

TABLE 2

Hydrogen Peroxide-Air Reclamations at 150-170° F.

RUN No.	LITHARGE CONTENT Pounds PbO/Gallon Doctor Solution					
	Original	½ Hour	1 Hour	2 Hours	3 Hours	Final
1A	0.035	0.079	0.084	0.086	0.090	0.093
2A	0.038	0.085	0.087	0.087	0.093	0.112
3A	0.050	0.093	0.098	0.102	0.104	0.106
4A	0.093	0.106	0 108	0.114	0.114	0.114
5A	0.071	0.083	0.088	0.100	0.106	0.112
6A	0.045	0.059	0.072	0.072	0.077	0.077
Average	0.0563	0.0841	0.0895	0.0935	0.0973	0.1023

Average charge spent doctor solution: 10,520 gallons.
Average time of reclamation: 3½ hours.
Average quantity hydrogen peroxide added, per reclamation: 39.7 lbs. 100 vol. (28 percent by weight).
Time of addition of hydrogen peroxide: 15-20 minutes, included in time of reclamation in table above.

TABLE 3

General Characteristics of the Doctor Solution Under Study (From analyses performed on reclaimed doctor)

1.

Color	Wine-red
Odor	Good
Gravity, ° Baume, corrected to 60° F.	21.0
Solid content, lbs./bbl.	62.16
NaOH content, lbs./bbl.	36.09
PbO content, lbs./bbl.	3.63
$Na_2S_2O_3$ content, lbs./bbl.	10.5
Other solids, by difference, lbs./bbl.	11.94

2.

Color	Wine-red
Odor	Good
Gravity, ° Baume, corrected to 60° F.	21.8
Solid content, lbs./bbl.	65.10
NaOH content, lbs./bbl.	46.50
PbO content, lbs./bbl.	2.86
$Na_2S_2O_3$ content, lbs./bbl.	7.98
Other solids, by difference, lbs./bbl.	7.76

The soluble-lead contents of the various solutions were obtained by titrating 10 c.c. of the doctor solution with a standard sodium sulfide solution, which was daily compared with a synthetic doctor solution of known litharge content. Sodium nitro-prusside solution was used as an outside indicator, and the endpoint determined by the first appearance of a purple color in the indicator which persisted for one second. The analytical method was checked a number of times against the ammonium molybdate method of lead analysis recommended in textbooks, and was found to be generally more accurate for plant determinations, where the presence of red oils and other extraneous matter in the titrated solution obscures the yellow color of the tannic-acid indicator of the molybdate endpoint.

Owing to changes in operating procedure at the treating plant over which it was not possible to exercise control, the soluble-lead contents of the "spent" doctor solution would naturally vary from hour to hour and from day to day, depending on the mercaptan content of the sour gasoline, the volume ratio of doctor to gasoline and other factors. It was therefore impossible to secure doctor solutions of identically the same composition for comparative tests. For purposes of evaluation of the effect of hydrogen peroxide on the reclamation characteristics of doctor solution at the plant where these tests were made, a group of 12 regenerations with air, and 6 regenerations with hydrogen peroxide and air have been grouped and averaged to secure, if possible, an overall picture of the effect of adding hydrogen peroxide to spent doctor solution at the outset of a reclamation, as compared with the ordinary method of air revivification.

For comparative purposes, therefore, the mode of operation in the regeneration step with hydrogen peroxide may be considered as identical with that in normal air operation save for the addition of approximately 40 pounds of 100 volume (28 percent by weight H_2O_2) hydrogen peroxide to each of the peroxide reclamation runs. The result of this addition is to increase immediately the soluble-lead content of the solution, although not in any stoichiometric relation; moreover, the rate of conversion of the lead sulfide to oxide is greatly enhanced, and the final soluble-lead content of the doctor solution is greater in the cases where hydrogen peroxide has been added than where air alone has been used. This is especially interesting in view of the fact that the potential lead contents of the solutions (determined by adding nitric acid to samples of the spent solutions containing PbS, and determining $PbCrO_4$ gravimetrically) showed an average available lead content (as PbO) of 0.111 pounds litharge per gallon. However, prolonging the air reclamations to 6 and 7 hours yielded only slight increases in soluble PbO content, by no means comparable with the increases shown in the case of hydrogen peroxide-air reclamation.

A comparison of the total quantity of litharge reclaimed by each method is naturally of interest,

and can best be shown by the accompanying tabulation:

	Air Reclamation	Hydrogen Peroxide-Air Reclamation
Original soluble lead content (from averages)	0.0535 lbs. PbO/gal.	0.0563 lbs. PbO/gal.
Final soluble lead content (from averages)	0.0823 lbs. PbO/gal.	0.1023 lbs. PbO/gal.
Total Gain lbs. PbO/gal.	0.0288	0.0470
Hydrogen peroxide added, lbs. 100 volume, average	none	39.7
Increased litharge content with hydrogen peroxide-air reclamation		0.0192 lbs. PbO/gal.
Volume of doctor thus treated (average)		10,520 gallons
Increased litharge formed, peroxide air reclamations (average)		202 lbs.

In the cases reported in Table 2, there was also a time saving in reclamation varying from 30 minutes to 2½ hours, depending on the stock reclaimed, which is reflected in corresponding savings in steam and air. In most refineries an accurate check on the quantity of each used for reclamation is not available, and only in the larger plants where these charges are budgeted to various departments, is any data at hand on these costs of operation.

The economic value of any process to the refiner naturally lies in its providing the same material or its equivalent at a cheaper price than it can be obtained in other ways. If we then evaluate this process on the basis of new or replacement litharge, based on present market prices of about $0.072 per pound, delivered at the point of operation, we arrive at the following conclusions:

The addition of 39.7 pounds of 100-volume hydrogen peroxide results in the formation of 202 pounds of litharge in each reclamation, in addition to that which would be formed in the normal air reclamation. At present market price, this would be worth $14.54.

The cost of the hydrogen peroxide used, based on a price of 18 cents per pound, 100-volume, would amount to $7.15 representing a net saving of $7.39.

The actual cost of reclaiming this additional quantity of litharge (due to peroxide reclamation) is $0.0354 per pound of PbO formed, which at the litharge contents indicated in the preceding tables compares very favorably with other methods of reclamation. In the particular cases in hand, it was virtually impossible to reach this litharge level by other means of reclamation, and the increase in litharge resulting from the addition of hydrogen peroxide could be compared directly with the cost of fresh PbO.

It is believed that the use of hydrogen peroxide in doctor reclamation will materially reduce overall chemical treating costs. For example, one tank of air-reclaimed doctor solution was sufficient to sweeten approximately 2000 barrels of sour gasoline (average mercaptan content, 0.0176 percent sulfur as mercaptan by weight). Each barrel of reclaimed doctor was therefore contacted with approximately 8.2 barrels of sour gasoline with a consequent decrease in the litharge content from 0.0823 to 0.0535 pounds PbO per gallon (verified by experiment, also see data, Table 1). The monthly chemical treating costs for a gasoline of this type was found to be $0.007 per barrel.

Considering this same sour gasoline treated with peroxide-air-reclaimed doctor solution, and adjusting the treating plant in such a way as to produce spent doctor of nearly the same litharge content as before (see data, Table 2), it can be calculated, as well as shown in operation, that the same volume of peroxide-reclaimed doctor will treat, instead of the 2000 barrels of gasoline, actually 3265 barrels of this same gasoline. These figures can be checked from the data given in the foregoing paragraph and Tables 1 and 2.

Assuming an equal rate of replacement chemicals in the two cases (obviously, this will not be true, as less replacement PbO will be needed in peroxide-reclaimed doctor) we arrive at the following figures.

Treating costs (chemicals) with air reclaimed doctor solution (from plant data) 2000 bbls. @ $0.007 per bbl.		$14.00
Treating costs using hydrogen peroxide		
Cost of hydrogen peroxide	$7.15	
Replacement chemicals (same as above)	$14.00	
	$21.15	
Volume treated with peroxide reclaimed doctor solution		3,265 barrels
Treating cost, per barrel gasoline		$ 0.00646

Since a portion of the replacement chemical costs was for fresh litharge, and this consumption was cut appreciably by the use of hydrogen peroxide, it is obvious that treating costs can actually be brought to a lower level by hydrogen peroxide-air reclamation of spent doctor.

From observations made on fresh litharge consumption, it is believed that the process is economically attractive to refiners using any quantity of this material for replacement purposes. The increased rate of reaction and higher litharge contents reached during hydrogen peroxide reclamation lessens the frequency of reclamation, thereby cutting down on mechanical losses encountered in such handling of the doctor solution.

The equipment necessary for the introduction of hydrogen peroxide to a batch reclamation set-up such as was used in the foregoing work, is comparatively simple. A single aluminum pressure vessel, 16 inches in diameter and about 20 inches high, was used as a working container for the hydrogen peroxide. This vessel was equipped with a flanged head for inspection and cleaning purposes, and the requisite inlets and outlets for hydrogen peroxide, a pressure gage, and a compressed air line.

Concentrated hydrogen peroxide in the proper quantity was charged to this container, diluted with approximately two parts of water, and the resultant mixture forced by air pressure through a ¼-inch outlet line at the base of the container to a ¼-inch iron pipe distributing line which was attached to a ¼-inch iron perforated spider resting on the bottom of the reclamation tank. The rate of flow of the peroxide solution is adjusted by means of a special alloy needle valve so that the total time of addition is not less than 15 or more than 30 minutes.

It is necessary that the spent doctor solution be brought to the temperature of reclamation before

addition of the hydrogen peroxide, and it is imperative that the air stream be agitating the doctor solution as much as practicable during the addition of the peroxide, in order that localized action (simply oxidation of the suspended PbS in the system) be prevented in so far as possible. For the same reason, it is desirable to add the peroxide with 50-60 pounds per square inch air pressure on the peroxide vessel, to secure as widespread distribution through the air spider as possible.

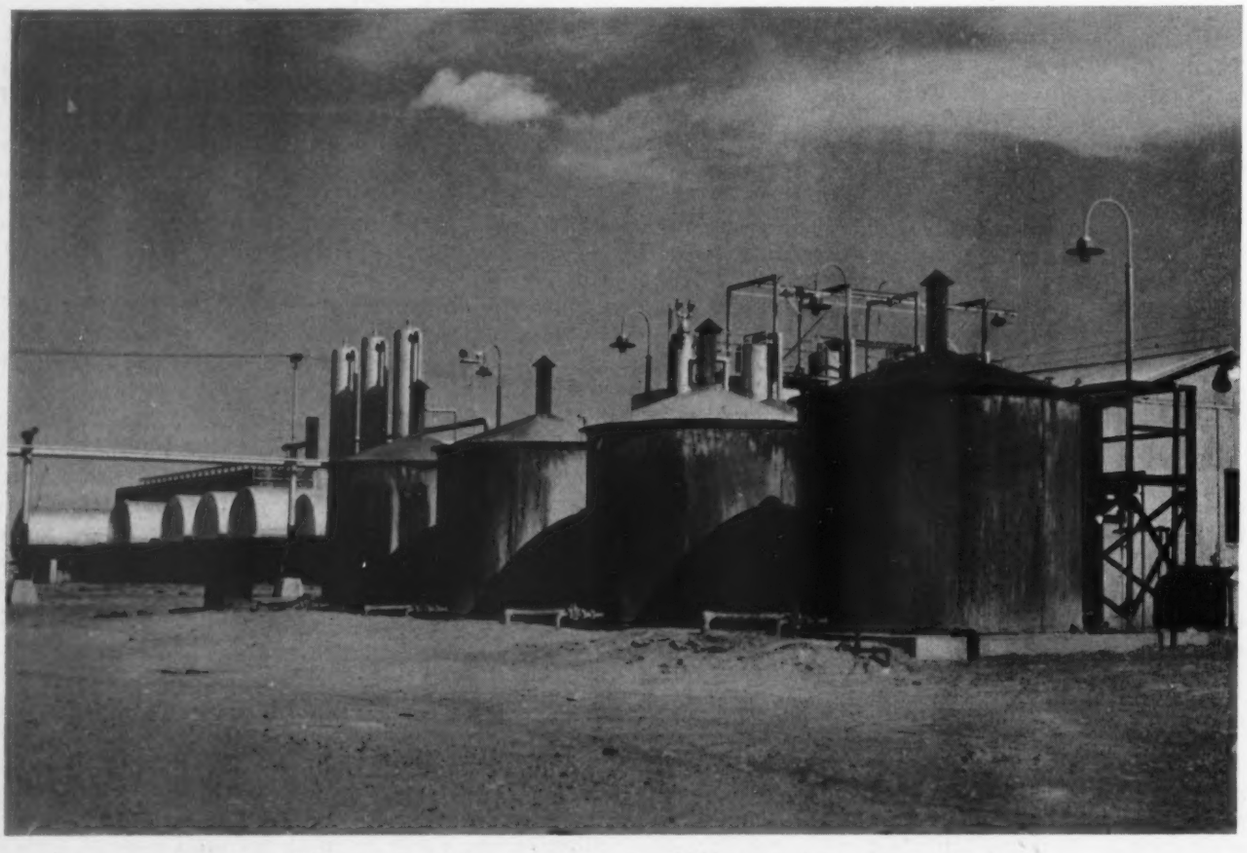
The optimum quantity of hydrogen peroxide to be added to a reclamation can be determined for a given set of conditions by comparatively simple experiments, but may vary over wide limits, depending on the operating conditions encountered within the plant itself.

Hydrogen peroxide has long been considered an expensive, unstable chemical. The developments in recent years in manufacturing methods and stabilizers make possible its use in large quantities without undue expense. Concentrated hydrogen peroxide will decompose in the presence of numerous catalysts, notable iron, copper, manganese or chromium salts. For this reason an aluminum pressure vessel is used as a primary container for the peroxide at the treating plant. For the same reason, it is shipped in one of three types of containers, depending on the quantity ordered: (1) Glass carboys containing 110 pounds net; (2) aluminum drums containing 250 pounds net, and (3), aluminum lined tank cars of 40,000 and 80,000 pounds capacity. All weights refer to 100 volume (28 percent) hydrogen peroxide. Under normal conditions of storage, the peroxide is stable over a period of years. The stability in use is such that contact with the iron distributing lines and spider gave no trouble from excessive decomposition of peroxide under the operating conditions described.

The labor required and the technique involved in the introduction of this oxidizing agent into treating systems is such that it may be safely entrusted to the regular treating plant operators. Since it leaves only water on decomposition, spillage or personal contact with the reagent does not constitute a hazard. Since it is a liquid, it may be measured conveniently by volume and handled with a minimum of effort.

It is virtually impossible in a report of this character to evaluate in general terms the applicability of the process to treating plants in general. Each treating plant and each reclamation problem present specific difficulties. The peroxide-air type of reclamation is sufficiently flexible to permit adaptation to practically any refinery operating condition. Laboratory and pilot plant work on doctor solutions from widely differing treating systems indicates that results similar to those described in the foregoing pages may be expected in almost every case.

Only in recent years have treating plants been given the attention and study they deserve, and it is hoped that the results published herein will stimulate further plant work on the improvement of doctor reclamation systems.



Typical doctor sweetening plant. Caustic and doctor solution storage tanks in the foreground.

Journal Lubrication

Friction Coefficients in the Thin Film Region

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and
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ABSTRACT

DATA are presented on the friction coefficients, seizure points and wear for partial journals. The apparatus was a modified Timken machine. Pressure varied from 800 to 23,000 psi and temperature from 70 to 400° F. Mid-Continent SAE 30 oil was used and the influence of 2-4-6 Trichlorophenol and Dichloromethylstearate as addition agents was studied. The important of the roughness of the bearing surfaces on performance is discussed. For steel bearings, Dichloromethylstearate materially lowers the friction and increases the seizure load, but wear also increases. A short review of other work on this subject is included.

THE modern trend in the use of most machinery is toward smaller, lighter and faster equipment. This calls for higher speeds and greater loads on bearings which must at the same time be reduced in size. Automotive and aircraft engines are good present-day examples. Yet the wear and the power loss due to friction through the use of these bearings must not be excessive. In fact it should be reduced. These requirements mean that the bearings must operate under conditions where factors other than the viscosity of the lubricant become important. Just what these factors are is not completely known, but one can easily visualize that with gradually increasing pressure or temperature, the lubricating films would become thinner and thinner until seizure occurred. This region of transition between full fluid lubrication and metallic contact is called the thin film region. It is probable that the film here is so thin that the cohesive forces of the metal surfaces can be transmitted across it. Also, due to the "rough spots" of the surfaces, there are probably many points of metal-to-metal contact long before seizure occurs.

From a practical standpoint the important items for consideration under the conditions just mentioned are the ability of the lubricant to prevent wear, its ability to prevent seizure, that is, its film strength, and a low power loss or coefficient of friction. Experimental data on thin film lubrication are few, but enough have been reported to permit some understanding in a qualitative way. McKee[8] and Bridgeman[1] have demonstrated that the performance with thin films depends on other properties than the viscosity. Their reports include plots of the friction coefficient as a function of the viscosity, speed, and load on the bearing, where speed is the important variable. The divergence of the curves in the thin film or boundary film region is attributed to oiliness. The definitions of oiliness, however, are quite vague, although many explanations have been offered[6].

Wear tests have been conducted by many workers. The most complete data seem to be those of Davis, et al[3] on cadmium, copper-lead and bronze bearings. The results show considerably less wear when an addition agent is added to the oil, but no correlation is attempted between the wear and any physical property of the oil. Undoubtedly the wear will depend on both the lubricant and the bearing material.

It has been known for many years that the addition of small amounts of fatty oils to a mineral oil would increase the ability of the latter to carry heavy loads, or the same load at higher temperatures. These addition agents are selectively adsorbed on the metal surfaces and are much more strongly held than the mineral oil alone. More recently, chlorinated esters have proved quite satisfactory in increasing film strengths[7]. The molecular orientation of these polar molecules has been thoroughly studied by X-ray diffraction methods[2]. But here again there is no apparent correlation between the film strength of the oil and any of its other properties. The authors have found from their own experience that the wear on the bearing may be excessive long before seizure takes place. In some instances, however, it may be desirable to let this extra wear take place, replacing the parts occasionally and taking advantage of the increased allowable pressure.

It is the purpose of this paper to present experimental data in the thin-film region and by controlling some of the known variables to find out, if possible, what are some of the unknown. Measurements have been made of the coefficients of friction, the loads under which seizure occurred, and the amount of wear under the conditions of test. Commercial oil was used in all work, some with addition agents. Data were secured with a Timken machine which had been modified to suit the need. The loads on the bearing

varied from 800 to 23,000 pounds per square inch; the temperature from 70 to 400° F.; and the speed was held approximately constant at 550 RPM. Corrections for both pressure and temperature were made in the viscosity of the oil films.

DETERMINATION OF COEFFICIENT OF FRICTION

The fundamental equation for power losses in journal bearings[9] is as follows:

$$W_f = 2\pi MN \quad (1)$$

where W_f is the work expended in friction, M is the moment of journal friction and N is the revolutions per minute. Also

$$M = fpr \quad (2)$$

where f is the coefficient of journal friction, p is the total load on the bearing in pounds and r is the bearing radius, or D is the diameter in feet. The normal pressure in pounds per square inch of projected area may be represented by P and the bearing width in inches by L. Then

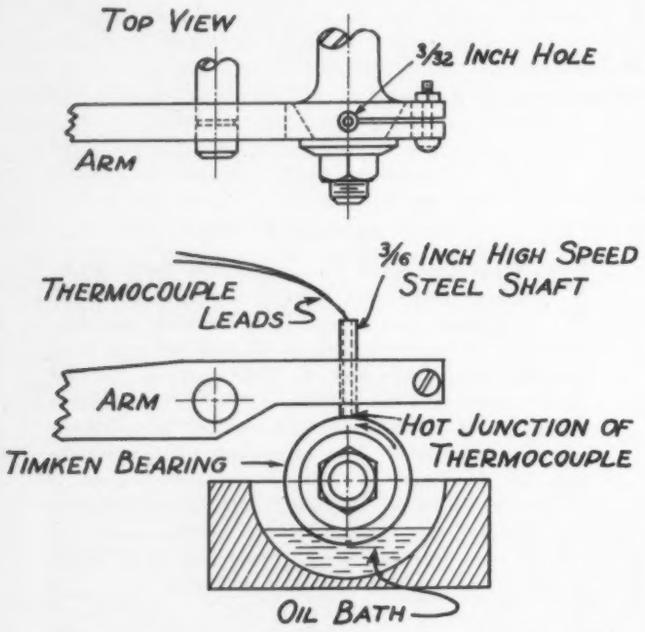

FIGURE 1

Diagram of Ring, Shaft and Thermocouple arrangement.

$$P = \frac{p}{2rL}, \text{ and} \quad (3)$$

$$W_f = 2\pi fprN = 2\pi f(P2rL)rN, \text{ or} \quad (4)$$

$$W_f = fSp \quad (5)$$

where S is the surface speed of the bearing in feet per minute. Equation 5 was used for the calculation of the friction coefficients in this work. Here W_f was measured with a wattmeter and converted to the proper units. It will be noted that while this equation gives absolute values for the coefficient of friction, it is perfectly general and tells nothing about the factors which may influence it, either relating to the bearing or the lubricant.

TEST APPARATUS

Timken rings were used in all tests. Pressure was applied to the rings by means of a high-speed steel drill shaft. This shaft was 3/16 inches in diameter and had been hardened at 2300° F. and quenched in oil, so that there was no appreciable wear on it, even after all of the tests had been made. The bottom of the shaft and ring is illustrated in Figure 1. Before hardening, a 3/32-inch hole had been drilled through the center of the shaft so that the hot junction of a thermocouple could be placed in contact with the oil film. A chromel-alumel thermocouple gave temperature readings with an accuracy of greater than 2° F. The weight arm (Figure 2) consisted of a steel arm and a weight platform to which from one to 20 weights could be added. This arm transmitted the load to the high-speed steel shaft in such a manner that the weight on the platform was multiplied 23.62 times. The projected area of the shaft was 0.0207 square inches, so that the weight platform when empty transmits 806 pounds per square inch to the ring. Each weight weighed 1 pound ($\pm$0.011 pounds) and transmitted 1142 pounds per square inch to the bearing. Thos, the greatest pressure obtainable was [806 + (20 $\times$ 1142)] or 23,646 pounds per square inch.

The ring, as it rotated, dipped into a cup which contained the oil sample. In this manner the oil film was cooled both by the oil sample and the air. No attempt was made to control the film temperature. Naturally it increased as the load was increased. The capacity of the oil cup was 22 cubic centimeters. This was thoroughly cleaned by washing in gasoline and petroleum ether before each test. A new ring was used for each run.

One of the chief limitations to the use of the Timken machine for comparing different oils has been the fact that the area of contact was variable. The use of the shaft arrangement shown here permitted tests to be made under constant area of contact and approximately constant speed. The maximum change in RPM for all tests from zero to maximum load was 7 percent. However, no assumption was made concerning the speed. It was measured with a "speed-counter" in every case. The film temperatures, while not controlled, were nearly equal in all runs for a corresponding load. A wattmeter, connected to the motor, was used to measure the change in power requirement with each weight addition.

The procedure consisted of running the motor, which rotated the test ring, with no load and recording the initial wattmeter reading and temperature.

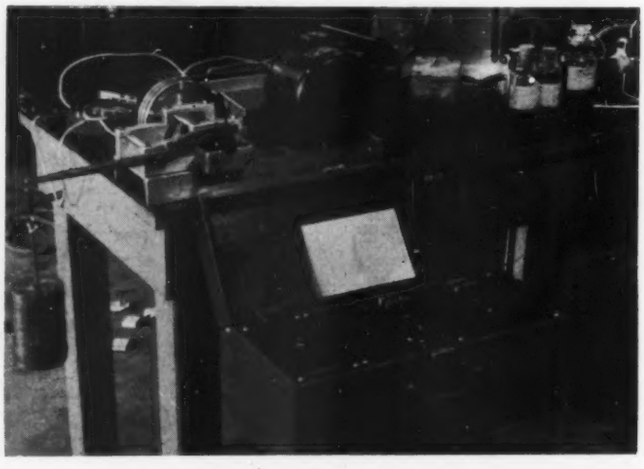

FIGURE 2

Arrangement of Apparatus.

Then the weight platform was suspended and the machine ran for two minutes. One weight was added at each two minute interval thereafter, meanwhile recording the watts and temperature for that period. This process was continued until the full load of 20 weights was added or the bearing seized.

The experimental determination of the amount of wear was carried out by using the exact procedure as that mentioned above. Bearings were weighed before and after each run to get the loss of weight in milligrams. For example, the determination of the wear at 6500 pounds per square inch started at zero load and continued until the arm and the 5 weights had been added at 2-minute intervals. The same procedure was followed for 8, 10, 15 weights, etc., so that each point on the wear curve represents a separate run.

VARIABLES INVOLVED IN THIN FILM LUBRICATION

The coefficient of friction is a function of a great many variables[6] among which the following are listed:

Z = The viscosity of the oil in centipoises.
N = Revolutions per minute.
P = Pressure in pounds per square inch of projected area.
C = Diametrical clearance in inches.
D = Diameter of bearing in inches.
L = Length (or width) of bearing in inches.
B = Surface condition or roughness factor.
a = Temperature coefficient of viscosity.
b = Pressure coefficient of viscosity.
h = Heat capacity of the oil.
k = Thermal conductivity of the oil.
E_1 and E_2 = modulus of elasticity of the journal and bearing.

Under the conditions of these experiments, that is, with the same oil and using Timken test rings, all of the variables except Z, N, P, B, a, and b should be constant for any given bearing load. Thus, we may write,

$$f = \Phi (Z, N, P, B, a, b) \qquad (6)$$

where Φ is some unknown function.

It has been shown that in the fluid film region that the coefficient of friction depends only on the viscosity of the oil (1,8), or

$$f = \Phi \left(\frac{ZN}{P}\right) \qquad (7)$$

These experiments were conducted at approximately constant temperature and with low pressures, so that the viscosity of the film would be substantially that of the main body of the oil. Accordingly, for our method of test, Equation (6) may be written as

$$f = \Phi \left(\frac{Z'N}{P}\right) \text{ (B)} \qquad (8)$$

Where Z′ is the viscosity of the film, or of the oil corrected for both temperature and pressure. It will be noticed that $\frac{ZN}{P}$ in the units used is not dimensionless, but that it may be made so by including a constant factor. By using the present units, the validity of the results is not affected and the numbers are easier to handle. Plotting f against $\frac{Z'N}{P}$ (Equation 8) should give information as to the effect of surface conditions of the metal on lubrication in the thin film region and tell something of its relative importance. That was the procedure adopted by the authors.

The oils used in these experiments along with their physical properties are shown in Table I.

CORRECTION OF VISCOSITY FOR TEMPERATURE AND PRESSURE

All viscosities of the oils used were determined with modified Ostwald pipettes. The values in centistokes were then converted to centipoises and Saybolt seconds. A description of the method as well as

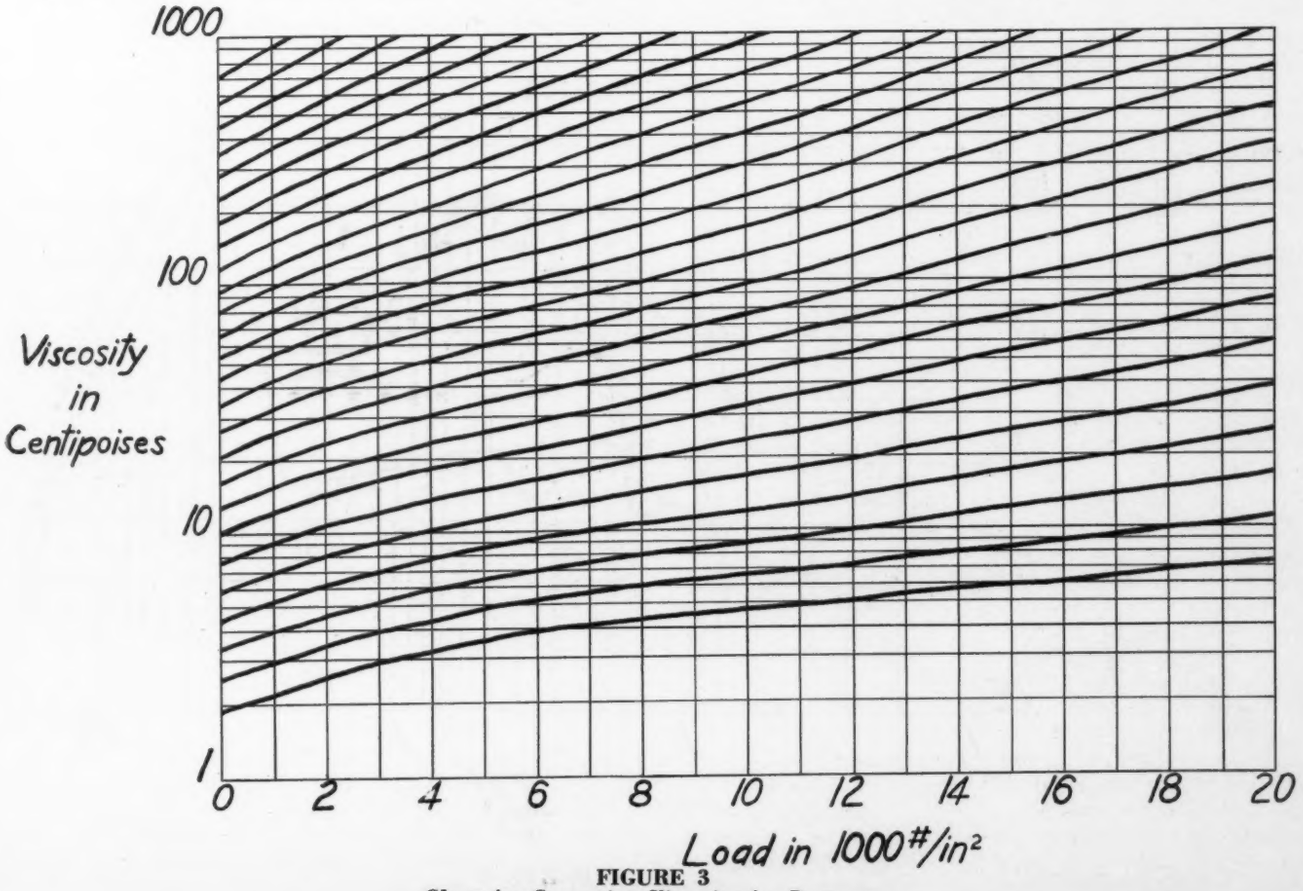

FIGURE 3
Chart for Correcting Viscosity for Pressure.

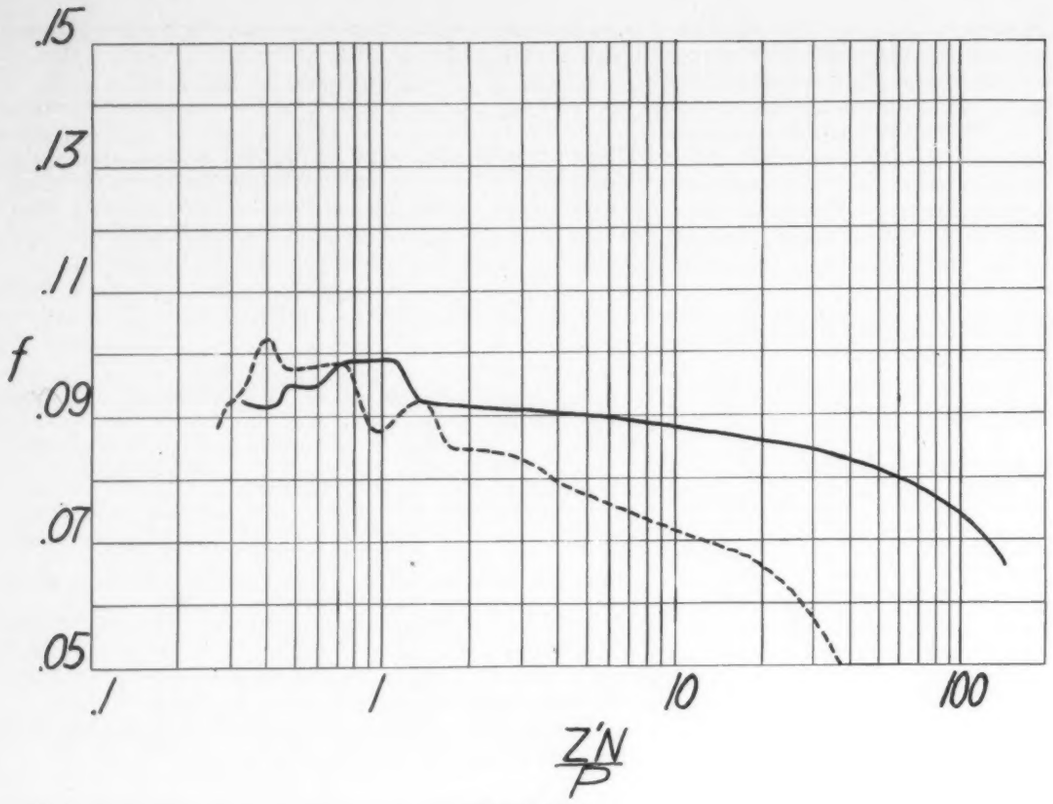

FIGURE 4
Friction Factors for Plain Mid-Continent Oil.

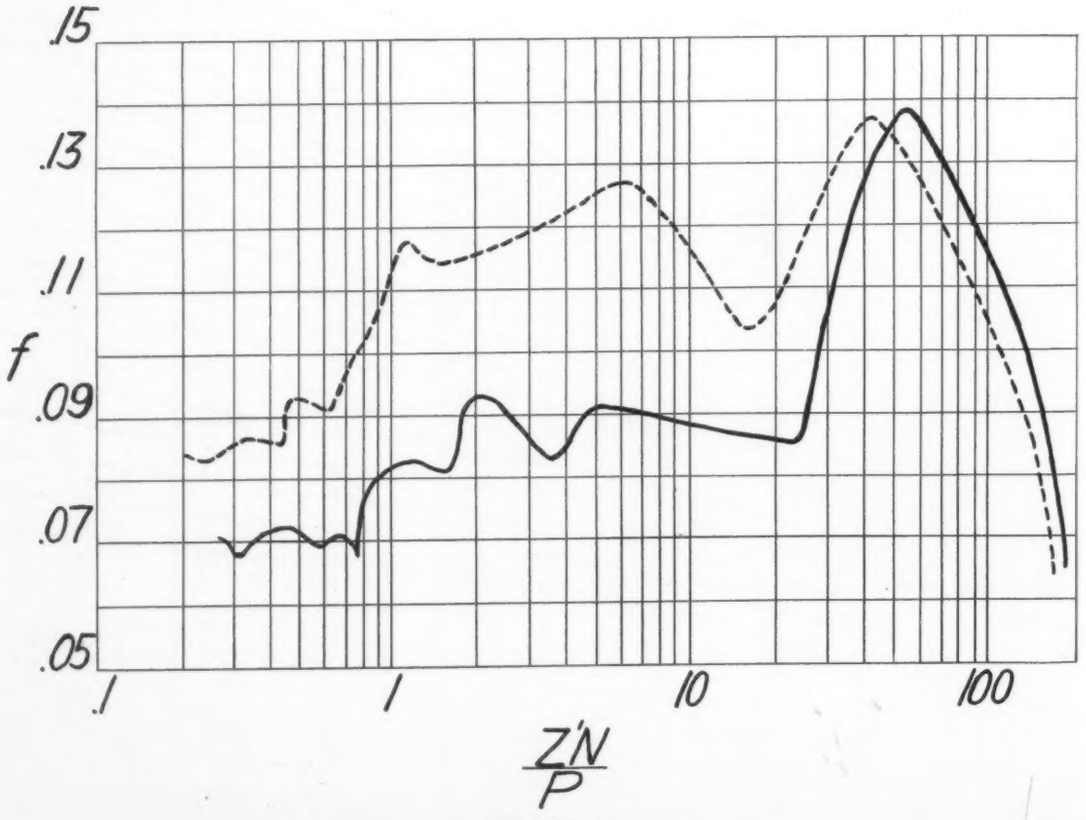

FIGURE 5
Friction Factors for Mid-Continent Oil with 2 percent Dichloromethyl Stearate added.

TABLE 1

Physical Properties of Oils Used

	A. P. I. at 60° F.	Saybolt Universal Viscosity, 100° F.	Saybolt Universal Viscosity, 210° F.	Viscosity Index
Oklahoma Oil (SAE 30)	26.2	578	63.2	77
Oklahoma Oil with 2 percent Dichloromethylstearate added	26.2	547	62.4	80
Oklahoma Oil with 2 percent 2-4-6 Trichlorophenol added	26.2	547	62.1	79

a table for converting centistokes to Saybolt seconds has been published.[10] The conversion of centistokes to centipoises at any given temperature is obtained by multiplying the centistokes by the density of the oil in grams per cubic centimeter at that temperature. The viscosity correction for temperature was read from Chart C, A.S.T.M. Tentative Standard D 341-37T.

Very few data are available on the effect of pressure on the viscosity of mineral oils. Dow[5] has found that at 20,000 pounds per square inch, the viscosity in centipoises increases 13 times for a Pennsylvania oil and 43 times for a California oil. He has also published some data on the variation of viscosity with pressure for Pennsylvania, Oklahoma and California oils at temperatures of 100° F., 130° F. and 210° F. The data differ widely for the three oils and at 26,000 pounds per square inch the viscosity of the Pennsylvania oil increased 25 fold, that of the Oklahoma oil 35 fold, and that of the California oil over 100 fold.[4]

The Oklahoma oil used by Dow was almost identical in viscosity with the one used in this work. By plotting the log of the viscosity against the load (using semi-log paper) the curves become approximately straight lines. Knowing also the variation of slope of these lines with temperature for the three temperatures given, it is possible to put in other lines covering the entire range of this work. The resultant chart is illustrated in Figure 3. Admittedly this is only an approximation, but the authors feel that it is the best method available for correcting for pressure at the present time. The maximum error should be considerably less than 10 percent. Similar charts have also been drawn for California and Pennsylvania oils.

CONSIDERATION OF RESULTS

Figures 4, 5 and 6 show the results from plotting coefficients of friction against $\frac{Z'N}{P}$ for the three oils used. That duplicate runs for any one oil do not check is at once apparent. Since all other conditions were held constant, it is evident that surface conditions of the ring play a very important part in the value of the coefficient of friction. The curves actually presented here are typical of many run in the authors' laboratory in the last three years. After this experience it is felt that any checking of two runs with the same oil would be mere coincidence. It will be observed that under loads of about 800 pounds ($\frac{Z'N}{P}$ values of about 160), the values for f are almost identical for all three oils. This load, then, must represent the beginning of the transition range from fluid film to thin-film lubrication. Since the roughness of these surfaces cannot be controlled, it is impossible to get relative comparison of the ability of the addition agents to lower the friction. However, it will be noticed that after a certain point is reached, there is a tendency for the addition agent

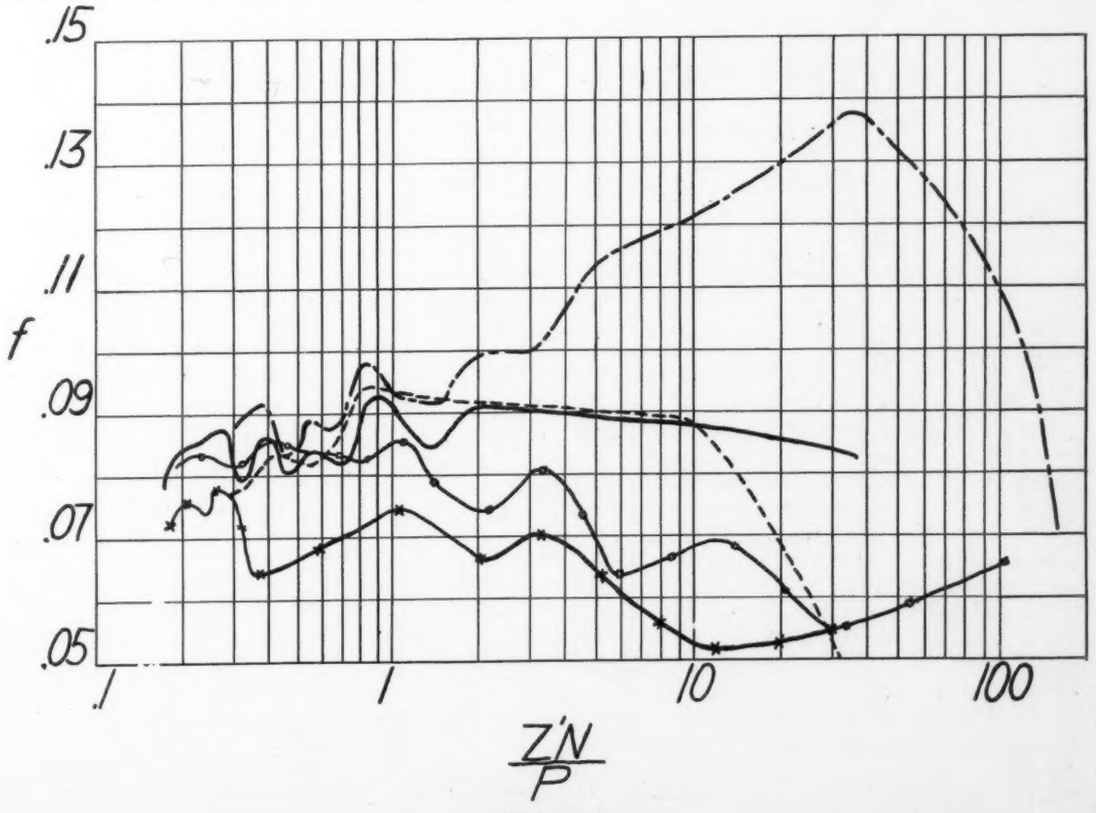

FIGURE 6

Friction Factors for Mid-Continent Oil with 2 percent 2-4-6 Trichlorophenol added.

TABLE 2
Seizure Loads of Oils (lbs./sq. in.)

Plain Oil	Oil with 2 Percent Dichloromethylstearate	Oil with 2 Percent 2-4-6 Trichlorophenol
17,900	> 23,600	> 23,600
19,000	> 23,600	19,000
19,000	> 23,600	16,800
13,300	> 23,600	23,600
19,000	> 23,600	16,800
20,200	> 23,600	16,800
13,300	> 23,600	> 23,600
11,100	> 23,600	23,600

to lower the coefficient of friction for any one bearing with increasing load and temperature. This is not true for the plain oil. It is important to point out that the friction factor for any given oil and bearing does not increase in value rapidly with temperature and pressure increase.

Further evidence of the influence of surface roughness is shown in Table 2. When the oil film breaks suddenly at a certain load, this point measured in pounds per square inch is called the "seizure load." These points are shown in the table. They are comparable to the film strengths but the test conditions are different. The load required to break the oil film varies considerably for the plain oil and for the sample with 2-4-6 Trichlorophenol added. Average results are higher for the latter, however. Dichloromethylstearate increases the ability of the oil to maintain loads up to the limit of the apparatus used. If higher loads could be applied, the results would probably be variable also. Thus, it appears that this addition agent is superior to 2-4-6 Trichlorophenol or no addition at all as regards the lowering of the friction factor and increasing the strength of the film.

The effect of the addition agent on the amount of wear on the rings is shown in Figure 7. Since these curves represent average results of several runs, they are probably fairly independent of surface roughness. Dichloromethylstearate causes the most wear and 2-4-6 Trichlorophenol the least of the three oil samples used. The authors have been unable to find any relationship between friction coefficient, or seizure load, and the amount of wear. Since there are so many possible variables, the function is undoubtedly complex. It should be emphasized that these results are only for steel on steel. There is evidence to show that these same addition agents behave differently for other bearing metals,[3] so far as the wear is concerned. It is realized that much more work must be done covering the entire range of pressure, temperature and speed before fundamental relationships can be developed.

ACKNOWLEDGMENT

Thanks are due to C. E. Winters, 65 Mountfort Street, Boston, Massachusetts, for valuable suggestions and to J. S. Hume of Continental Oil Company for furnishing the oils used.

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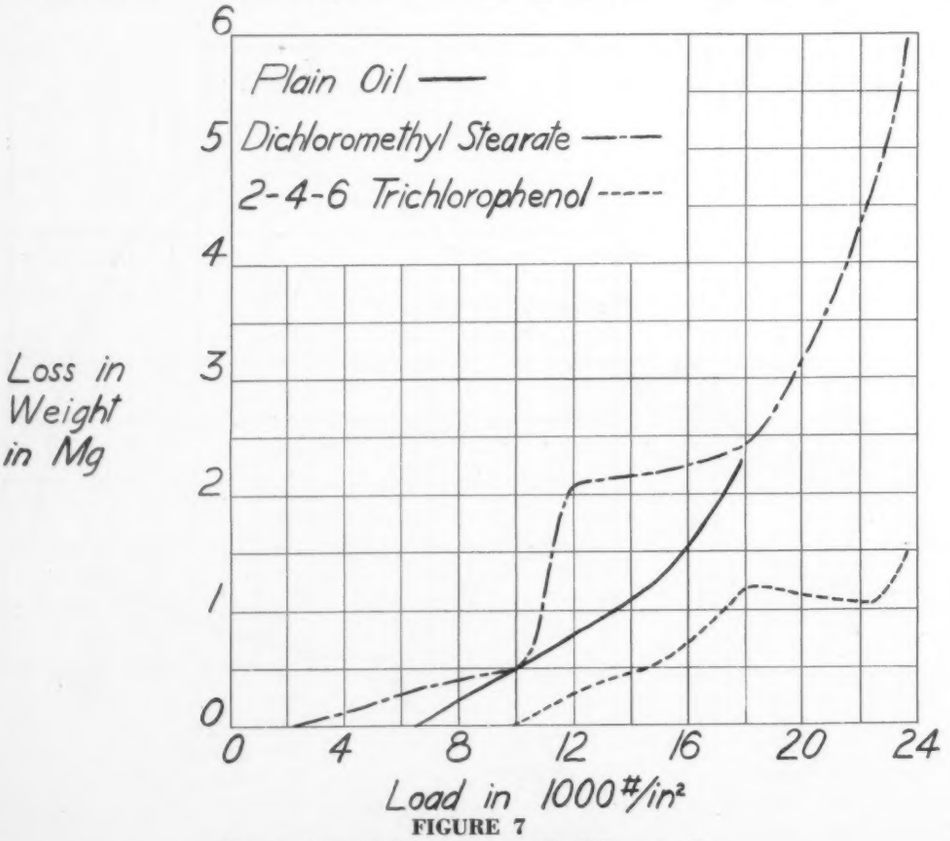
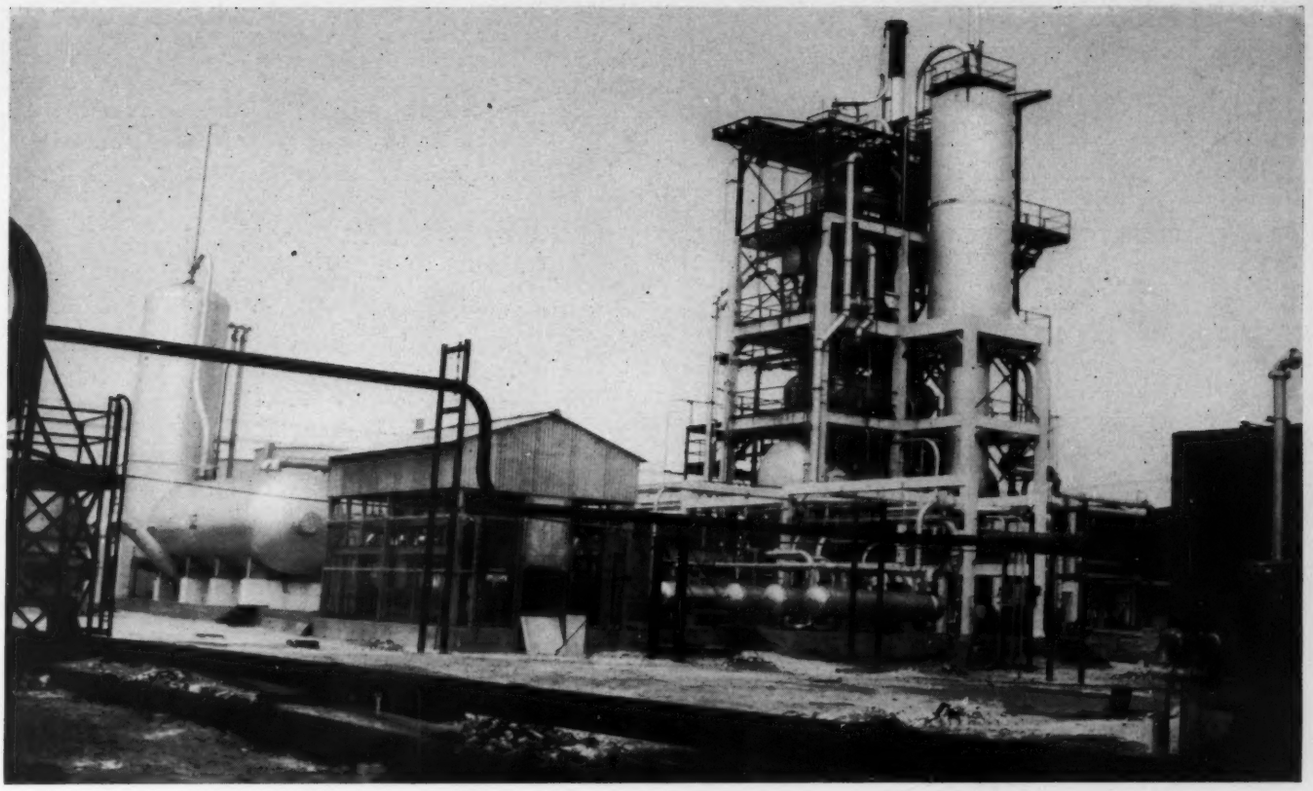


FIGURE 7
Comparison of Ring Wear with different oils.



Debutanizer and rerun unit for production of high octane blending gasoline.

Preparation of Blending Stock For 100-Octane Gasoline

L. J. COULTHURST
Foster Wheeler Corporation

AVIATION gasoline having a 100-octane anti-knock rating has become established as an economic reality within the last two years, and is no longer regarded as a laboratory curiosity. It has been estimated that 90 percent of the U. S. Army Air Corps aircraft fuel consumption for 1938 will be of the 100-octane grade, and there is no doubt that commercial planes will be using 100-octane motor gasoline exclusively in the very near future.

100-Octane aviation gasoline is usually prepared by blending about 50 percent of 70- to 76-octane, straight-run gasoline with 40 percent of commercial iso-octane, 10 percent of iso-pentane and a maximum of 3 cubic centimeters of tetraethyl lead per gallon.

Gasoline that is suitable for processing to 70-76-octane blending medium may be obtained from a number of sources but non-uniformity of the various gasolines requires considerable flexibility in the equipment for the production of the blending stock. One of the major refining companies has recently installed units with a high degree of flexibility for debutanizing and rerunning a considerable variety of stocks to produce 70-76-octane straight-run gasoline. The general arrangement of the debutanizer and rerun units for production of high octane blending gasoline is indicated in the accompanying flow diagram.

Straight-run gasoline is first processed in a debutanizer in which propane and excess butane are withdrawn overhead since these fractions are not desired in the aviation gasoline. Following debutanization the gasoline is fractionated in the rerun unit to produce a cut of the required boiling range.

The charge of straight-run gasoline is pumped through heat exchangers, wherein it is preheated by the debutanizer bottoms, and enters the tower near the middle. Adjustable weir-type bubble trays in the tower fractionate between the heavy bottoms and the undesirable propane and butane. The overhead, including propane and excess butane, is totally condensed in shell-and-tube water-cooled condensers and collected in a reflux tank. Part of the overhead fraction is recirculated to the top of the tower as reflux to produce the required fractionation. The net overhead product of propane and butane is pumped to a stabilizer wherein the butane is separated for ultimate use as a general blending medium.

The bottoms from the debutanizer tower are split

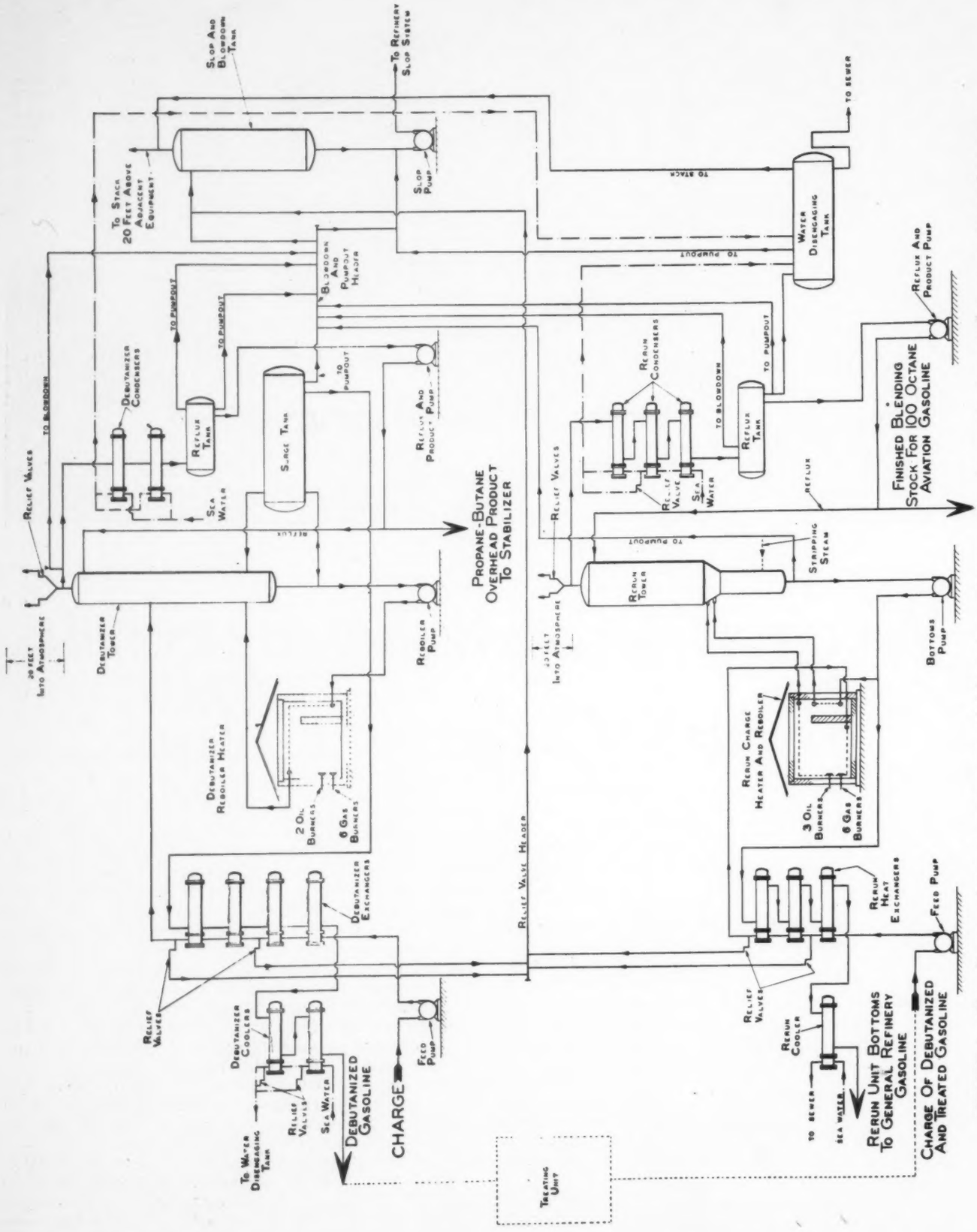


FIGURE 1—*Flow diagram showing arrangement of debutanizer and rerun units for production of high-octane blending gasoline.*

into two streams. One is pumped through a heater which vaporizes the lighter fractions to perform the stripping function in the lower section of the tower. The other stream, which ultimately forms a part of aviation gasoline, is piped to a surge drum. This drum "floats on the line" at the bottom of the debutanizer and receives, by gravity, any hot liquid that is not pumped through the reboiler. The surge drum performs two functions:

1. A quantity of liquid is constantly available for pumping through the heater tubes to prevent overheating.

2. Surge capacity is provided for subsequent intermediate treating operations.

The debutanizer bottoms leaving the surge drum pass through the heat exchangers mentioned above wherein they give up most of their heat to the incoming charge. They are further cooled by sea water in shell-and-tube coolers, before being processed in a treating plant.

After treatment, the debutanized gasoline is processed in a rerun unit in order to obtain the desired end point. First, it is pumped through heat exchangers wherein some heat is obtained from the tower bottoms and it is then passed through the radiant section of a heater. Extreme care is taken to avoid overheating the charge because of color specifications. From the heater, the debutanized gasoline is charged directly into the rerun tower.

In order to assure adequate stripping in the lower section of the tower, part of the bottoms are circulated through the convection section of the heater which serves as a reboiler. The vapors that are liberated, together with the stripping steam, make the unit capable of producing the maximum volume of desired blending stock. The same pump that forces the bottoms through the convection section of the heater, also delivers the net stripped bottoms through the heat exchangers and coolers to storage for ultimate use in general refinery gasoline.

The overhead from the rerun tower is totally condensed in shell-and-tube condensers and collected in a reflux tank. Part of the overhead is returned to the top of the tower as reflux to control the end-point. The remaining overhead product is the desired aviation gasoline blending medium which is pumped to storage for ultimate mixing with iso-octane and iso-pentane.

The requirements for steam are reduced to a minimum in this installation and it is used only for stripping in the rerun tower. The heaters are direct-fired, of the single-end type with six gas burners. In the debutanizer furnace, two additional oil-fired burners, employing mechanical atomization, are furnished as alternates. The heater for the rerun unit is similarly equipped for alternative oil firing except that three oil burners are used instead of two. All of the pumps are motor-driven with self-venting, vertically-split casings.

In all of the coolers and condensers the baffles are of Muntz metal, tube sheets of naval bronze, channels and covers of NiResist, and floating head covers of either bronze or NiResist. However, since the stock passing through the two debutanizer condensers is particularly corrosive, special precautions were taken for the protection of these units by using monel metal on the shells, ring flanges, nozzles, and shell covers.

The debutanizer and rerun units are designed for maximum safety and high "on-stream" time due to their great importance in the manufacture of 100-octane aviation gasoline. All heat exchangers, coolers and condensers are by-passed on both the shell and channel sides so that any one of them may be withdrawn from service for inspection or repairs while the other units continue to operate. After a heat exchanger has been out of service, there is the possibility of human error in that hot oil may be admitted to the shell while the cold side is full of oil and the valves are closed. The transmission of heat to the constricted cold oil would cause dangerous expansion and pressure on the channel side, if it were not for a ¾-inch relief valve that is provided on each heat exchanger. The condensers and coolers are also protected by relief valves. All major relief valves are installed in duplicate with an interlocking device in order that one will always be in service. Outlets from all relief valves are either extended 20 feet vertically to discharge to atmosphere or are piped to a relief valve header which conducts any vapors or oil directly to a blowdown drum. This drum, which is part of a complete blowdown system, is arranged for rapid relief of any or all of the pressure vessels by remote control through blowdown headers, and to collect slops from each tower whenever desired. Any liquid collected therein may be discharged to the general refinery slop system by means of a special pump.

Fire protection against possible leaks in the condensers and coolers is obtained by conducting all of the cooling water to a water-disengaging drum. Any vapors that may be present either here or in the blowdown drum are vented through a stack to the atmosphere at an elevation 20 feet above surrounding equipment.

The debutanizer and rerun units were designed to produce aviation gasoline blending medium from any one of three stocks as indicated in Table 1.

TABLE 1

Alternate Operations

	Case I Straight Run Naphtha	Case II Straight Run Naphtha	Case III Aviation Gasoline Base Stock Blended with Light Ends
Debutanizer Charge Stock			
Barrels per day	11,110		6,112
A. P. I. gravity	54.0		75.3
Reid vapor pressure	7.0		18.0
Initial boiling point, ° F.	108		.....
Percent at 140° F.	2.6		.....
Percent at 158° F.	4.8		.....
Percent at 176° F.	9.2		.....
Percent at 212° F.	20.7		.....
Percent at 257° F.	38.6		.....
Percent at 302° F.	58.6		.....
Percent at 356° F.	83.1		.....
Percent at 374° F.	90.6		.....
Percent at 392° F.	95.0		.....
End point, ° F.	401		.....
Propane, liquid volume percent	1.0		0.0
Butanes, liquid volume percent	.....		19.45
Iso-Pentane, liquid volume percent	.....		18.75
Debutanizer Overhead Product			
Barrels per day	244	500	1,598
Propane, liquid volume percent	45.5	22.2	.....
Butanes, liquid volume percent	54.5	77.8	70.3
Iso-Pentane, liquid percent	.....	.....	29.7
Total percent	100	100	100
Debutanizer Bottoms Product (Rerun Unit Charge)			
Barrels per day	10,866	10,610	4,514
Rerun Unit Bottoms			
Barrels per day	6,302	6,897	Negligible
A. P. I. gravity	46.2	43.2	.....
Rerun Unit Overhead Product (Aviation Gasoline Blending Stock)			
Barrels per day	4,564	3,713	4,514
Octane rating (anti-knock)	70–72	74–76	76
A. P. I. gravity	63.0	69.0	66.1
Reid vapor pressure	7.0 (max.)	7.0 (max.)	7.0
Initial boiling point, ° F.	111	111	105
Percent at 140° F.	4.5	9.0	10.0
Percent at 158° F.	13.0	24.2	29.0
Percent at 194° F.	38.5	67.0	62.0
Percent at 212° F.	55.5	86.0	77.0
Percent at 257° F.	89.0	97.0	95.5
End point, ° F.	290	265	295

This is a finished stock ready for blending with commercial iso-octane and iso-pentane to produce 100 octane aviation gasoline.

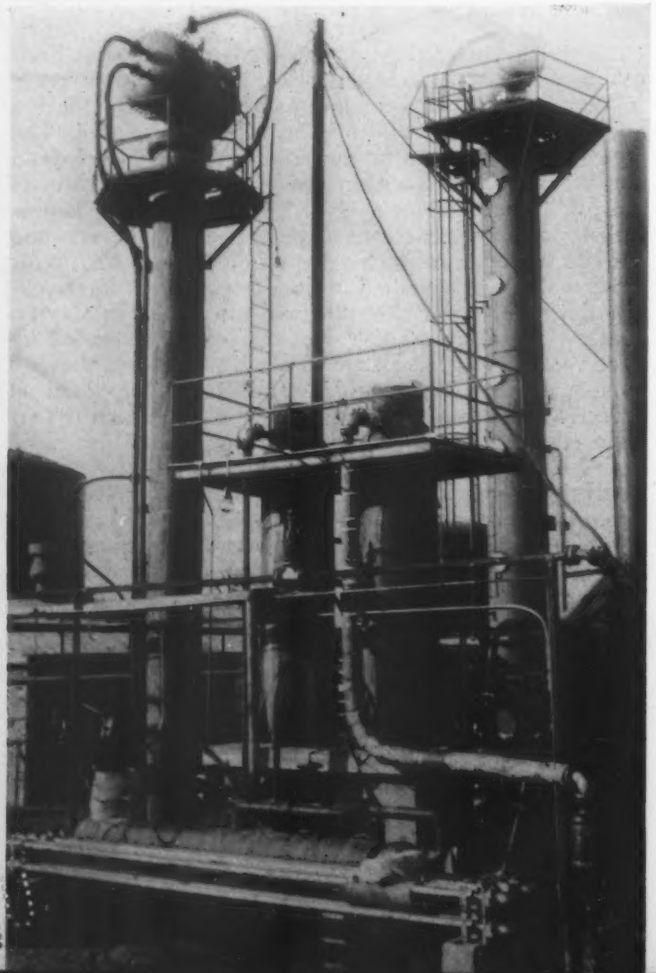
Catalytic Polymerization . . .

at Johnson Oil Refining Company Plant

Wm. J. LEENHOUTS
Superintendent

A NEW Universal Oil Products Company non-selective polymerization unit, modern equipment for making high-octane gasoline and increasing yield, has just been put into operation by Johnson Oil Refining Company at Cleveland, Oklahoma. The plant was built by the owner from plans and specifications furnished by the licensor. About two years ago the company put in a new Dubbs selective cracking plant by which it was possible to make 70-72-octane cracked gasoline from topped crude. Now it has made this further improvement of installing a new polymerization plant which will make gasoline of 82-85 octane and this polymer gasoline has a blending value with straight-run gasoline of 110 to 120 octane.

Showing condensers, coolers and reboiler in foreground and catalyst towers, heater and stabilizer towers.



In polymerization we take the small gaseous molecules and bring them together under the proper conditions of low temperature and high pressure so that they will react to make a new and larger molecule of high octane value and belonging to the gasoline boiling range. In the cracking process gases are produced which formerly were burned under the stills for fuel. In order to produce a high-octane gasoline by cracking, a breaking down of the higher-molecular hydrocarbons must take place and gas is produced as a by-product. This gas is used in the process of making polymer gasoline.

The cracking plant stabilizer is operated so as to drive off all C_3 and most of the C_4 hydrocarbons. In our selective type cracking plant the gases from the stabilizer yield about 45 to 47 percent propene C_3H_6, and butenes C_4H_8 hydrocarbons. The propene and butene hydrocarbons are convertible in a catalytic polymerization plant. The gasoline yield is increased approximately 3 percent and this in turn reduces crude requirements about 6 percent for the same quantity of gasoline.

A compressor is used to feed the gases to the poly plant at a pressure of about 500 pounds. The compressor is a 6x16-inch single-action gas compressor, equipped with adjustable unloader and run by a 12x16-inch 50-horsepower Diesel engine. The normal capacity of the compressor is 800,000 cubic feet per day at a temperature of 150° F., 180-pound suction pressure and 500-pound discharge pressure.

The compressor discharges the gas at about 180°F. to the furnace where it is heated to about 325 to 400° F. While the catalyst is new the gases are being heated to about 325° F. and this temperature will be increased up to 400° F. as the activity of the catalyst decreases. The furnace is a cylindrical shell 6 feet in diameter and lined with 4 inches of cement insulation. The 2-inch coil through which the gas passes is spiral in form and is set about 3 inches from the wall of the furnace and winds up in a nest coil in the top of the furnace. The gas comes in at the top of the furnace coil and goes down through the furnace coil counter-current to the flue gases coming up. The furnace heater is equipped with a diaphragm control valve, operated by means of a temperature controller, making the temperature control of the furnace automatic.

From the furnace the gas passes to the catalyst

towers. There are two catalyst towers 30 inches in diameter and 15 feet 6 inches long by 15/16-inch wall thickness, good for an operating pressure of 500 pounds at 500° F. The catalyst towers are filled with a solid phosphoric acid catalyst.

In these towers when the gases contact the catalyst the temperature increases approximately 110° F. due to the exothermic reaction which takes place. The greater part of the reaction takes place in the first tower and the increase of temperature is about 90°F. The increase in temperature in the second tower is only about 20° F. The temperature of the polymer gasoline after it leaves the catalyst towers is about 440° F. and the conversion is now complete. The towers are operated at about 500 pounds pressure. The elevated pressure gives a high capacity of polymerization and a maximum throughput. The conversion of olefins over the first 30-day period has run about 98 percent.

The chemical changes which take place in polymerization cannot be confined to a few most desirable reactions, namely, of combining two molecules of C_3 and C_4 series to make a gasoline molecule of C_6, C_7 or C_8 series.

A great number of products may be produced. The most simple of these reactions would be:

Ethylene C_2H_4 plus Propylene C_3H_6 = Pentenes C_5H_{10}
Propylene C_3H_6 plus Propylene C_3H_6 = Hexenes C_6H_{12}
Propylene C_3H_6 plus Butylenes C_4H_8 = Heptenes C_7H_{14}

These simple reactions do not represent even a small part of the reactions that take place. When it is considered that the new product formed may be a combination of any two or more of the above simple molecules it can be seen how complicated the reactions may be. If the conditions of reactions are not carefully controlled the resulting product might even be fuel oil or tar. Although the greater percentage of gas will react to form the desired polymer gasoline, conditions must be carefully controlled; otherwise, there will be an over-polymerization of some of the products going through the catalyst towers.

HEAT EXCHANGER OR POLYMER CONDENSER

After leaving the catalyst tower, conversion of the gases to polymer is complete and the polymer gasoline, together with butane and propane, the unconverted gases, are passed to the polymer condenser. The hot polymer and gases pass through the shell of the condenser counter-current to water going through the tubes and is cooled to about 180° F., at which temperature it is sufficiently cooled to enter the stabilizer tower for stabilizing.

The stabilizer tower is 24 inches in diameter by 30 feet 6 inches long and ½-inch wall thickness and is operated at 275-300 pounds pressure. The top temperature of the stabilizer tower is maintained by a condenser of the shell-and-tube type, the hot gases passing through the shell counter-current to the cool water through the tubes. The tubes are of Admiralty metal and are ¾-inch in diameter. This condenser maintains a top temperature of about 118° F. The bottom temperature of the stabilizer tower is maintained by a reboiler which operates at a temperature of about 270° F.

The fractionation of the polymer gasoline is known as stabilization or bringing the converted and recovered gasoline to the desired vapor pressure. This stabilization is accomplished by operating the tower at a bottom temperature of 275° F. and a top temperature of 120° F. and a pressure of 270 pounds, which is high enough to permit condensation of the desired hydrocarbons with a removal overhead of the light hydrocarbons which would exist as a gas at ordinary temperatures and pressures.

In stabilization the propane gases are driven off from the polymer gasoline, retaining as much butane as seasonal requirements will permit. The polymer gasoline is later mixed with the deep stabilized cracking plant gasoline of 5- to 6-pound vapor pressure and all the normal butane possible is utilized. Polymer gasoline from 10- to 30-pound R.V.P. can be produced, according to the product desired and to meet the seasonal demand.

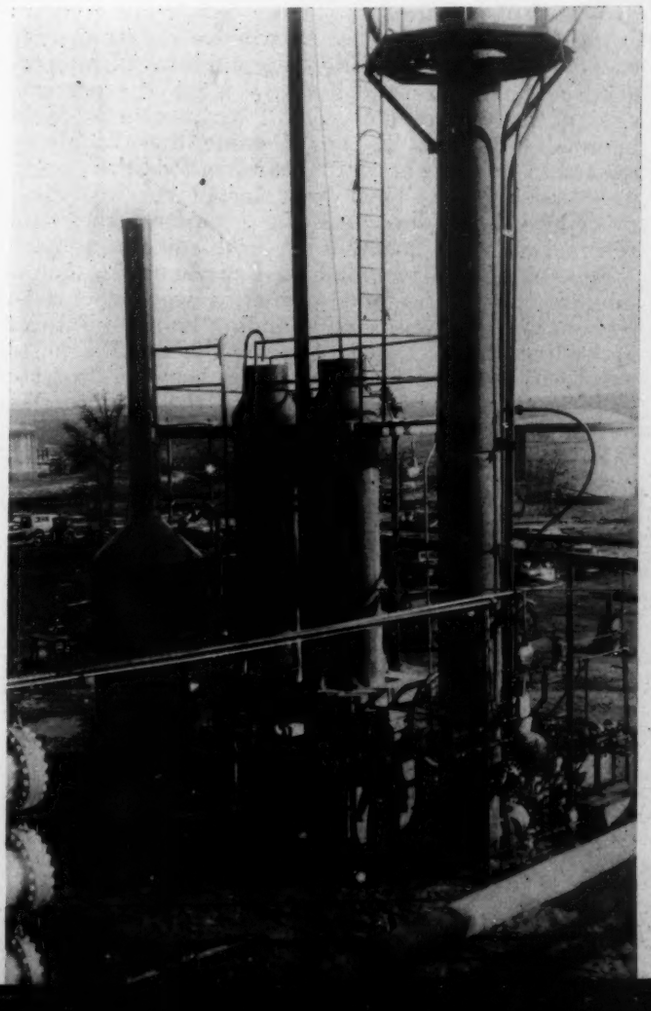
STABILIZER BOTTOMS COOLER

The stabilized polymer gasoline is drawn from the bottom of the stabilizer through a stabilizer bottoms cooler. The hot polymer gasoline passes countercurrent to cold water and leaves the cooler at a temperature of 70° F. ready for storage.

The polymer gasoline is mixed with the other cracked gasoline and is sweetened by the usual doctor process. So far polymer gasoline has shown a gum content of between 2.5 and 3.0 mgs.

The yield of polymer gasoline is a daily average of approximately 3300 gallons, or 3 percent, of 10-pound R.V.P. material, or 5300 gallons, or about 5 percent, of 30-pound R.V.P. About 10 gallons of 10-pound Reid polymer is produced for each 1000 cubic feet of fresh gas charged.

Showing from right to left: Heater, 2 catalyst towers, stabilizer.



A Method of
Gasoline Analysis

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G. W. STANTON
and
EUGENE WATKINS
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THE following describes an accurate method of gasoline analysis consisting only of fractionation, bromide-bromate titration, and determining index of refraction and gravity, which yields the ratio of branched to n-paraffins, the amount of unsaturation, and percentages of aromatics, naphthenes, and aliphatics.

The following method of gasoline analysis was first used in 1931 incidental to finding the possibilities in directing cracking reactions toward certain classes of compounds. Preliminary thermodynamic study showing that a naphthene is favored by pressure in preference to an olefin of the same molecular weight, that pressure favors n-paraffins in preference to branched paraffins, that high temperature favors aromatics, etc., made it seem worthwhile to analyze gasolines made under different conditions of temperature and pressure and see how much the percentages of the different classes of hydrocarbons could be made to vary. To be of value these analyses needed to be more accurate than methods then being used would give. Thus was started the analytical procedure here described for obtaining the data selected as most useful for a problem of this sort.

Several of the recommended methods for determining unsaturates and aromatics were compared by running tests on gasoline and on known mixtures of hydrocarbons. Figure 1 gives the results on 10 gasolines obtained by the Francis bromide-bromate test[1] compared to absorption in con H_2SO_4 as carried out in the Babcock butter-fat test bottle. A study of this curve shows that one method is in error in rough proportion to the percentage of unsaturates, but errors up to 20 or 30 percent are to be expected even after making some sort of empirical correction. A fifty-fifty mixture of 2-pentene and n-hexane gave results about 30 percent high on olefin by absorption in H_2SO_4 by method of Faragher, Morrell, and Levine[2]. The same mixture tested about 50 percent low using concentrated acid in the Babcock bottle. Francis' bromide-bromate test[2] gave answers as accurate as the volume measurements on this and other mixtures. A partial explanation of the errors in absorption methods is that different gasolines have different proportions of the different types of olefins and these are dissolved to a different extent from a mixture with other hydrocarbons. Another point noticed was that in dissolving an active olefin like butadiene, other less active olefins seemed to be carried along with the butadiene so that their rate of solution was increased many fold.

A test sometimes used for aromatics, nitration, recrystallization, and weighing, gave low results. The error was obviously due to loss in the rather long process. A much shorter, more accurate method involving calculation from gravity and index of refraction was discovered by one of the authors of this paper. Of interest is a somewhat similar method since described by Kurtz and Headington[3]. They,

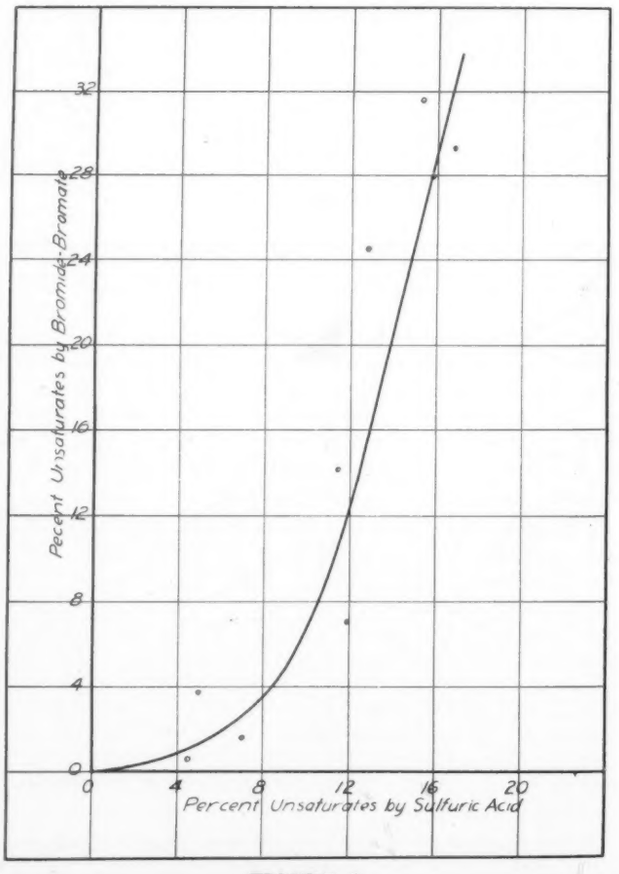

FIGURE 1
Comparison of Sulfuric Acid and Bromide-Bromate Methods for obtaining unsaturates in gasoline.

[1] Francis, J. Ind. Eng. Chem., 18, 821 (1926).
[2] Faragher, Morrell, and Levine, Ind. Eng. Chem., Anal. Edition 2, 18 (1930).
[3] Kurtz and Headington, Ind. Eng. Chem., Anal. Ed., 9, 21 (1937).

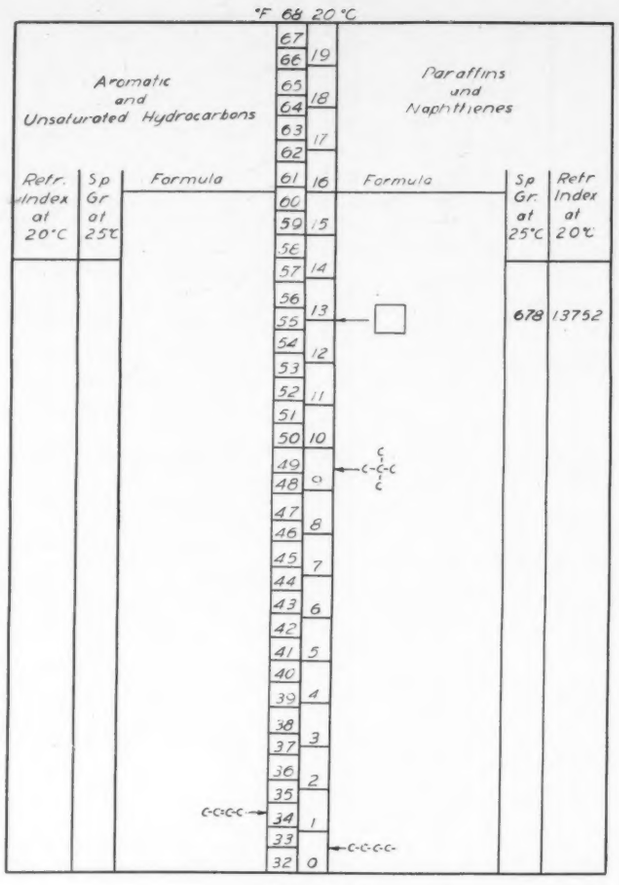

FIGURE 2

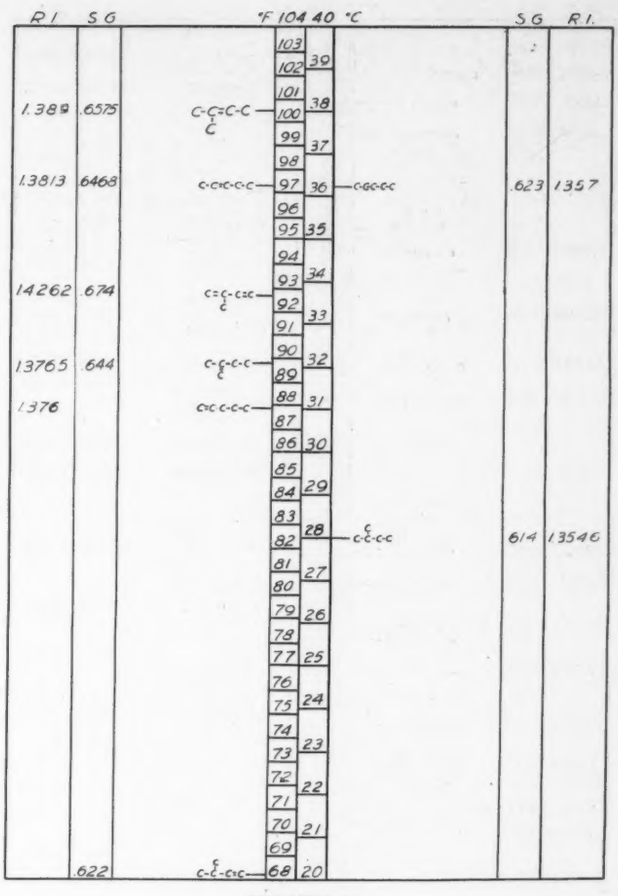

FIGURE 3

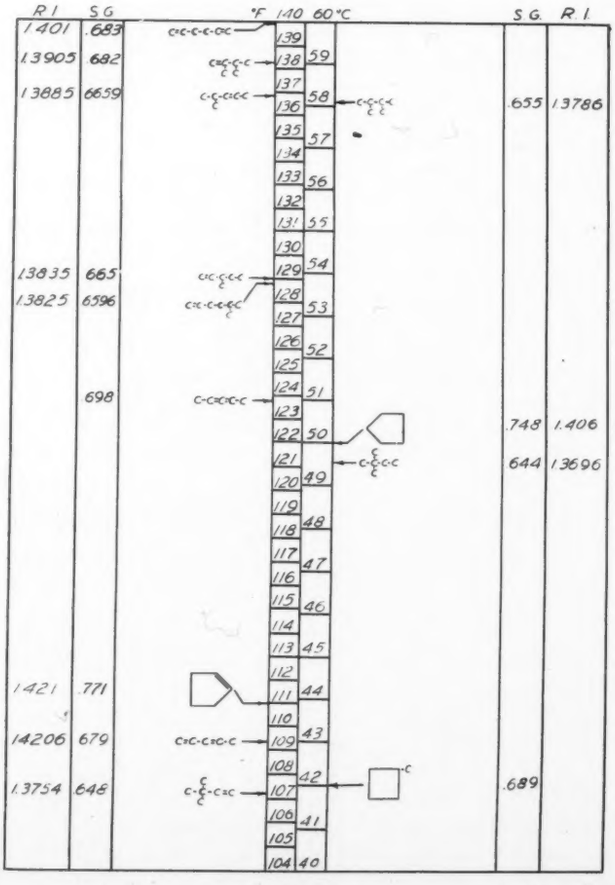

FIGURE 4

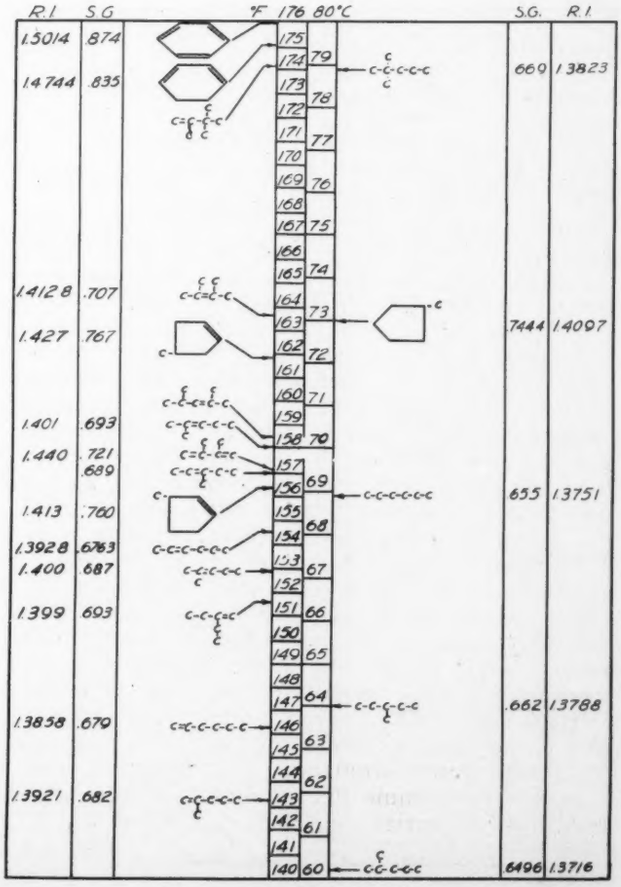

FIGURE 5

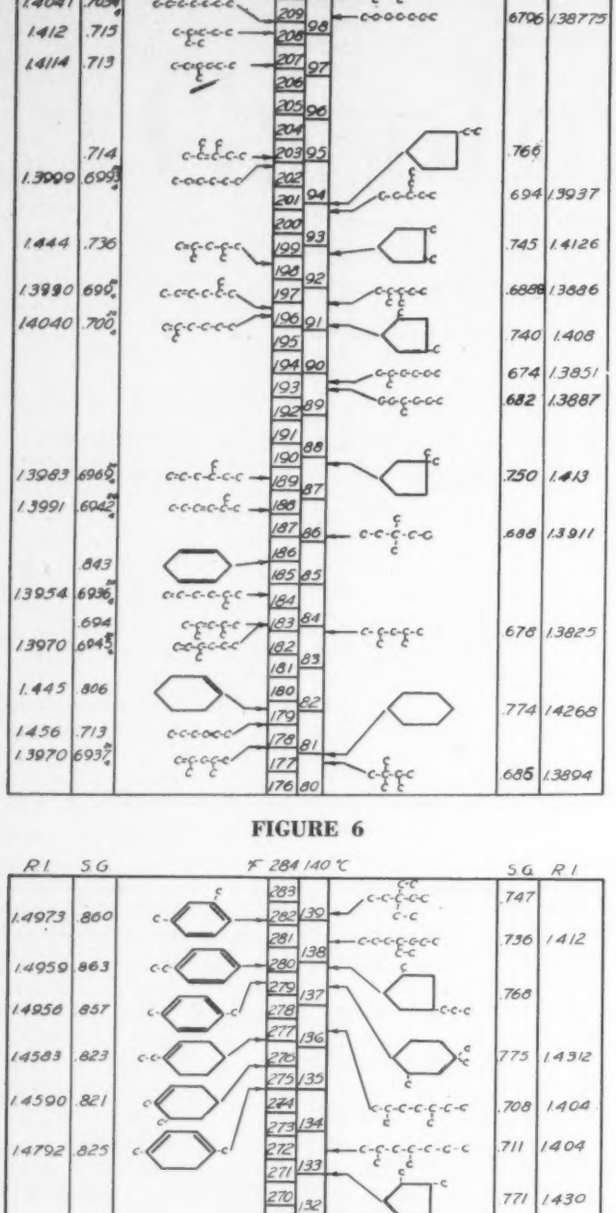

FIGURE 6

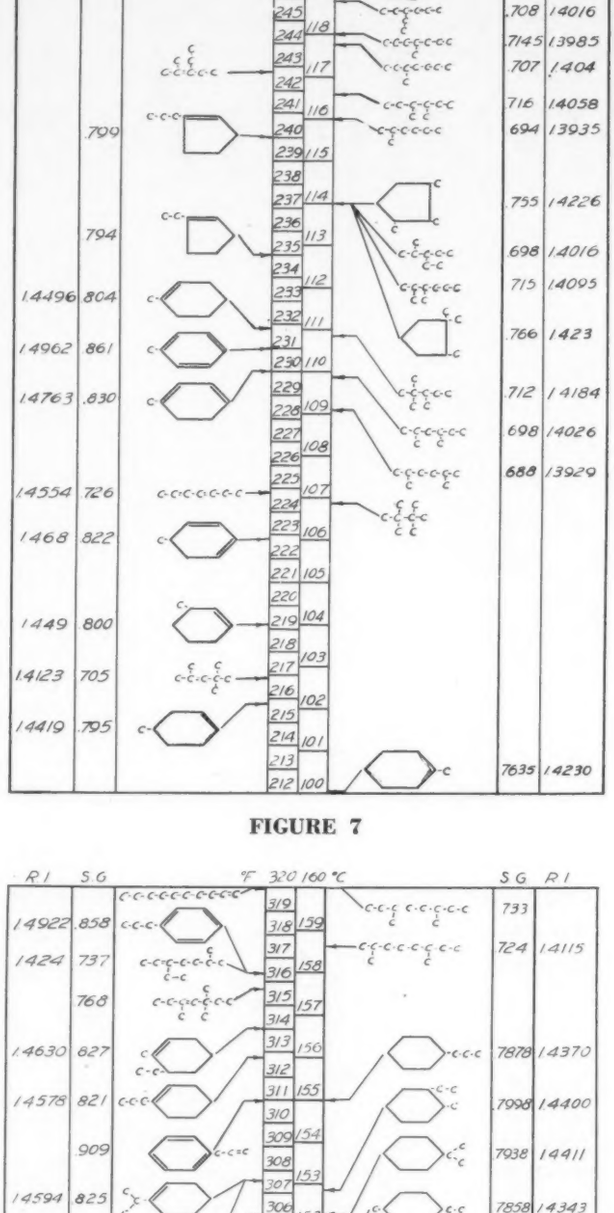

FIGURE 7

FIGURE 8

FIGURE 9

however, still used sulfuric acid absorption for the sum of olefins and aromatics.

DATA ON HYDROCARBONS

In order to construct curves for use in the analysis, it was necessary to compile all the physical data obtainable on the components of gasoline, namely, hydrocarbons. Every source available was searched. The results are given in figures 2 to 13 inclusive. The discrepancies found in the published data were surprising. It seems that the imperfect methods of purification gave rise to results which were off as much as 0.01 in the specific gravity and 0.005 in the index of refraction. In most such cases the latest published data was taken unless there was some reason for thinking it unreliable.

CONSTRUCTION OF CURVES USED IN THE ANALYSIS

Figure 14 was made by plotting specific gravity at 25° C. (77° F.) vs. index of refraction at 20° C. (68° F.) from the data given in Figures 2 to 13. To shorten its construction on a larger scale the following points are given as the best present data. For aromatics at 80° C. (176° F.) use index of refraction 1.5014, and specific gravity 0.874. The average for the other aromatics in the gasoline range is so near that of toluene, the point for toluene is recommended for all aromatics boiling above 110° C. (230° F.). This point has an index of refraction of 1.4962 and specific gravity of 0.861. The following table gives points on the paraffin line and the naphthene line.

PARAFFIN LINE				NAPHTHENE LINE			
° F.	° C.	Gr.	Ind. Ref.	° F.	° C.	Gr.	Ind. Ref.
140	60	.6525	1.3728	122	50	.7480	1.4060
158	70	.6600	1.3776	158	70	.7444	1.4097
176	80	.6690	1.3823	176	80	.7740	1.4268
194	90	.6780	1.3870	194	90	.7500	1.4125
212	100	.6865	1.3914	212	100	.7635	1.4230
230	110	.6950	1.3957	230	110	.7620	1.4225
248	120	.7030	1.3999	248	120	.7700	1.4260
266	130	.7105	1.4038	266	130	.7740	1.4285
284	140	.7170	1.4071	284	140	.7780	1.4310
302	150	.7225	1.4100	302	150	.7820	1.4330
320	160	.7275	1.4126	320	160	.7860	1.4350
338	170	.7325	1.4152	338	170	.7890	1.4367
356	180	.7370	1.4175	356	180	.7920	1.4384
374	190	.7415	1.4198	374	190	.7950	1.4400
392	200	.7455	1.4220	392	200	.7975	1.4415
410	210	.7495	1.4240	410	210	.8000	1.4428

In analysis of gasolines it is recommended Figure 14 be plotted on a larger scale using the data as given in above table and as given in Figures 2-13. Figure 14 as shown here is an illustrative figure only.

For parts on the lower end of paraffin line or naphthene line, and especially when using good fractionation, data for individual hydrocarbons should be used.

Figure 15 gives some recommended empirical corrections on specific gravity and index of refraction. These corrections allow for expansion on mixing of two or more types of hydrocarbons. These corrections were obtained by analyzing various known mixtures by the methods described in this paper and choosing corrections which would give the right answer. Further study of known mixtures, especially those containing branched chain compounds and 5 carbon rings, may indicate further revision of these corrections.

Two and three component mixtures of benzene, toluene, ethyl benzene, cyclohexane, cyclohexene, n-hexane, n-heptane, and n-octane and gasoline cuts were made and analyzed. As examples, a fifty-fifty mixture of aromatics and naphthenes analyzed 45

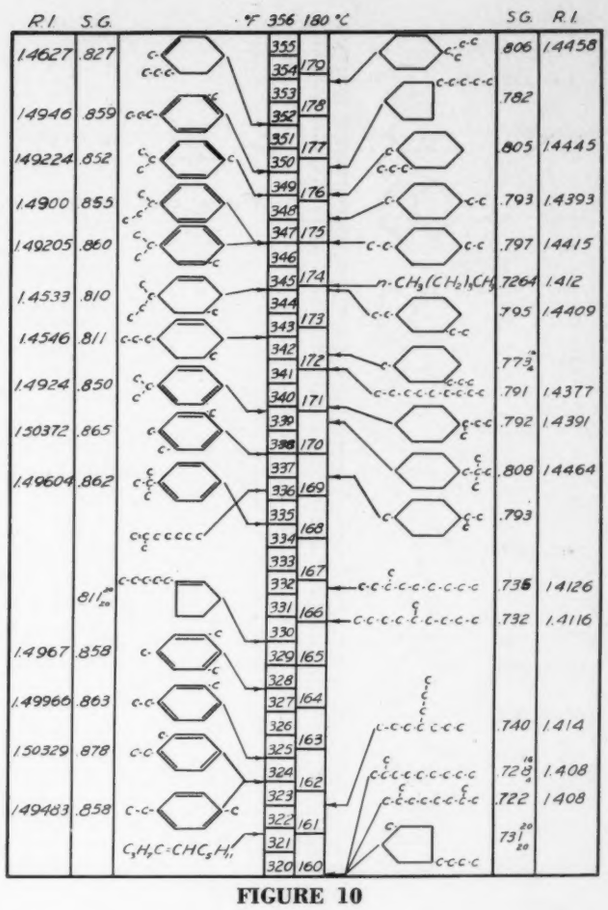

FIGURE 10

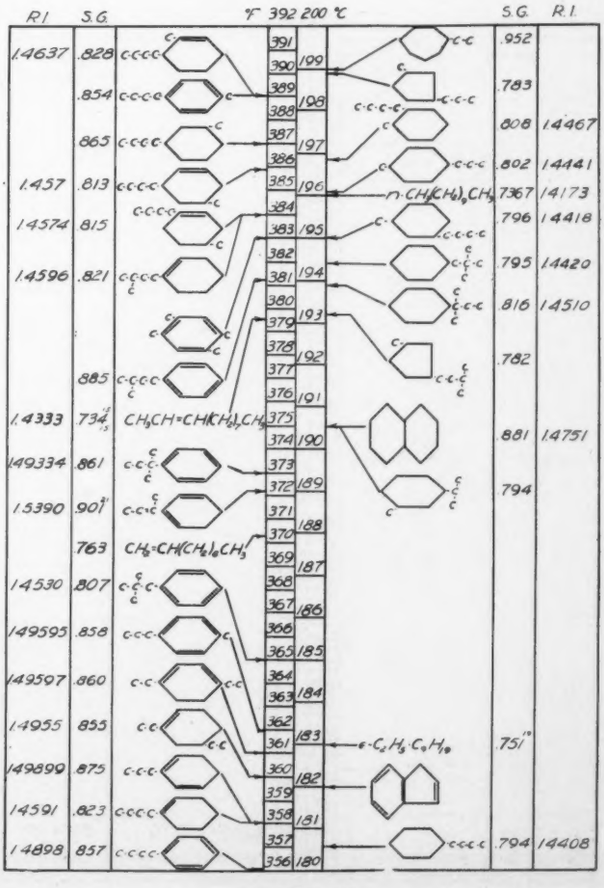

FIGURE 11

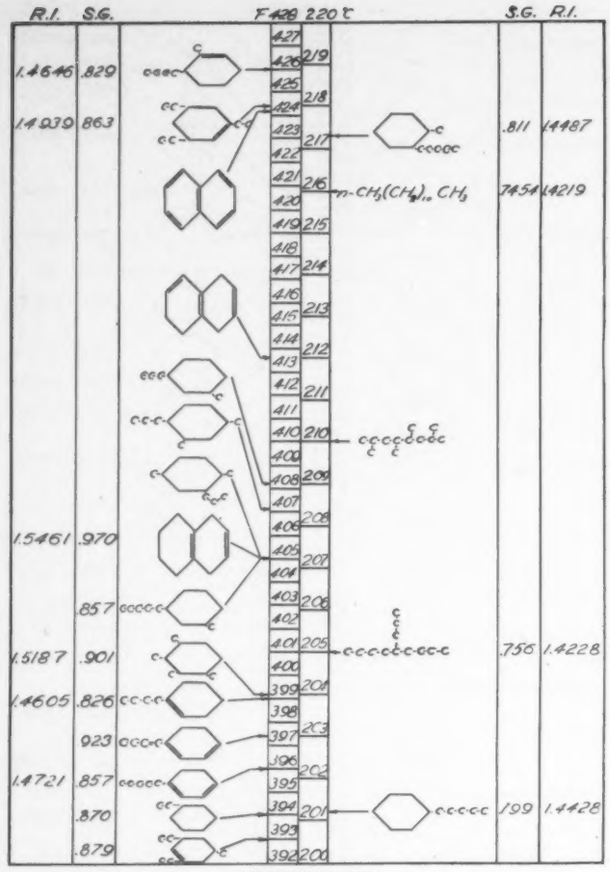

FIGURE 12

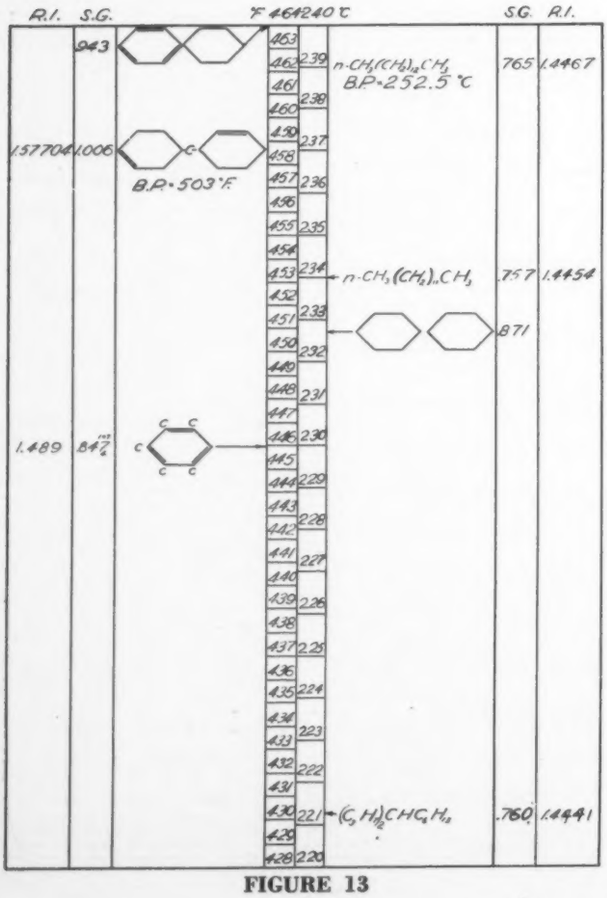

FIGURE 13

percent aromatics without the corrections. A 49.25 percent naphthene, 49.25 percent paraffin, and 1.5 percent aromatics analyzed 47.5 percent naphthene, 52.5 percent paraffin and 0 percent aromatics without the corrections. Figure 15 gives recommended average corrections based on this and similar data. It might be noted that present data indicates when benzene is the aromatic the corrections should be larger.

EXPERIMENTAL PROCEDURE

Experimentally, the analysis consists of fractionating a measured sample, and on each cut determining the volume, the index of refraction at 20° C. (68° F.), the specific gravity at 25° C. (77° F.), and amount of unsaturation by a bromide-bromate titration. In the fractionation, the lower-boiling cuts are taken so as to separate the branched-chain paraffins from the n-paraffins. In general if one desires to improve the accuracy, better fractionation will be used and narrower cuts taken. Starting with dry ice and acetone in the reflux condenser and main condenser and catching the first gases in an aspirator bottle gives data for the propane and butane cuts. However, starting with ordinary ice and catching the propane and butane cuts together over water may give sufficient data on the lower cuts. The ratio between branched and straight-chain aliphatics will ordinarily be the least accurate figure in the analysis. For gasolines showing less than 50 percent unsaturates the error here should be less than 5 percent in the 5-, 6-, and 7-carbon-per-molecule range if a fractionating column of 15 theoretical plates is used. When unsaturation goes up or there is less fractionation, the error becomes larger. Usually it will be found advisable to stop fractionation at approximately 150 to 160° C., the residue being treated as one cut.

The bromide-bromate titration used is an adaptation of the Francis method[1]. It was run in an evacuated bottle instead of in an Erlenmeyer flask. For the low-boiling cuts up to about 130° C. no noticeable error occurred if all the sulfuric acid was added at one time and then the bromide-bromate added in portions to excess. This shortened the time to about 2½ minutes for a titration. With the higher-boiling cuts it is necessary to follow the Francis method closely.

CALCULATION OF RESULTS

The amount of unsaturation for each cut was calculated from:

$$\text{Double bonds per mol} = \frac{V\ M}{2000\ v\ D}$$

where

V = net volume of 1 normal bromide-bromate used
M = average mol weight of gasoline cut (estimated from boiling point, Figures 2 to 13, and knowledge of hydrocarbons present).
v = volume of sample used in the titration.
D = specific gravity of the sample at room temperature.

The amounts of aromatics, naphthenes, and aliphatics in each cut are calculated as follows: The gravity and index of refraction are corrected for unsaturation by multiplying the double bonds per mol by 0.0208 and subtracting this result from the measured index of refraction, and by multiplying double bonds per mol by 0.0254 and subtracting this result from the measured specific gravity. These corrected values are then further corrected by adding corrections shown on Figure 15. The final values are then

plotted on Figure 14, locating a point. The following distances are then measured either perpendicular or parallel to the paraffin line:

m = distance from corrected point to paraffin line (give plus sign if on same side of line as naphthenes and minus sign if on same side as aromatics).
n = distance from naphthenes of same boiling point as the cut to the paraffin line.
a = distance from aromatics of same boiling point as the cut to the paraffin line.

The above three are measured perpendicular to the paraffin line. The following three are measured parallel to the paraffin line.

p = distance from corrected point to paraffins of same boiling point as the cut.
n′ = distance from naphthenes of same boiling point as the cut to paraffins of same boiling point.
a′ = distance of aromatics of same boiling point as the cut to paraffins of same boiling point.

Calculation is then made by solving the simultaneous equations:

$$nN - aA = m$$
$$n'N + a'A = p$$
$$\text{and } A + N + P = 1$$

where

N = volume fraction of naphthenes in the cut.
A = volume fraction of aromatics in the cut.
P = volume fraction of aliphatics in the cut.

ILLUSTRATIVE CALCULATIONS

Data on a cut with average boiling point of 130° C. showed for 5 cc. sample, 10 cc. of 0.458 N bromide bromate used and 3 cc. of 0.12 N $Na_2S_2O_3$ to measure excess. Specific gravity at 25° C. = 0.7470 and index of refraction at 20° C. = 1.4197. From Figure 8 one molecular weight is estimated at 120. Net amount of 1 N bromide bromate is $10 \times .458 - 3 \times .12 = 4.22$

$$\text{Double bonds per mol} = \frac{4.22 \times 120}{2000 \times 5 \times .747} = 0.0678.$$

Specific gravity corrected for unsaturation = .7470 — .0678 × .0254 = .7453. Index of refraction corrected for unsaturation = 1.4197 — .0678 × .0208 = 1.4183.

Plotting these values roughly on an enlarged Figure 14 (drawn from data in Table I, using 1 inch = .01 units of specific gravity and index of refraction) and noting that this point falls very nearly halfway between paraffin point at 130° C. and naphthene point at 130° C., the specific gravity and index of refraction are further corrected by adding .0012 to each as indicated on Figure 15. Final corrected specific gravity = .7453 + .0012 = .7465 and final corrected index of refraction = 1.4183 + .0012 = 1.4195. Plotting these final values accurately on the enlarged Figure 14 and measuring distances as indicated in above directions gives: m = 6.8 mm., n = 18.5 mm., a = 33 mm., p = 98.0 mm., n′ = 169 mm., a′ = 445 mm., then substituting in equations: 18.5 N — 33 A = 6.8, 169 N + 445 A = 98, and A + N + P = 1. Solving, naphthenes = 45.3 volume percent, aromatics = 4.8 volume percent, and aliphatics = 49.9 volume percent. These answers can then readily be changed to actual number of mols of each type of hydrocarbon by using total volume of original cut, specific gravities at room temperature, and molecular weights as estimated from Figures 2 to 13.

The authors wish to thank H. C. Crawford, John Merritt, Winton Rochelle, Otho Allen, and other chemical engineering students at Texas Technological College who have helped with the preparation of pure compounds and with testing of the method using these compounds.

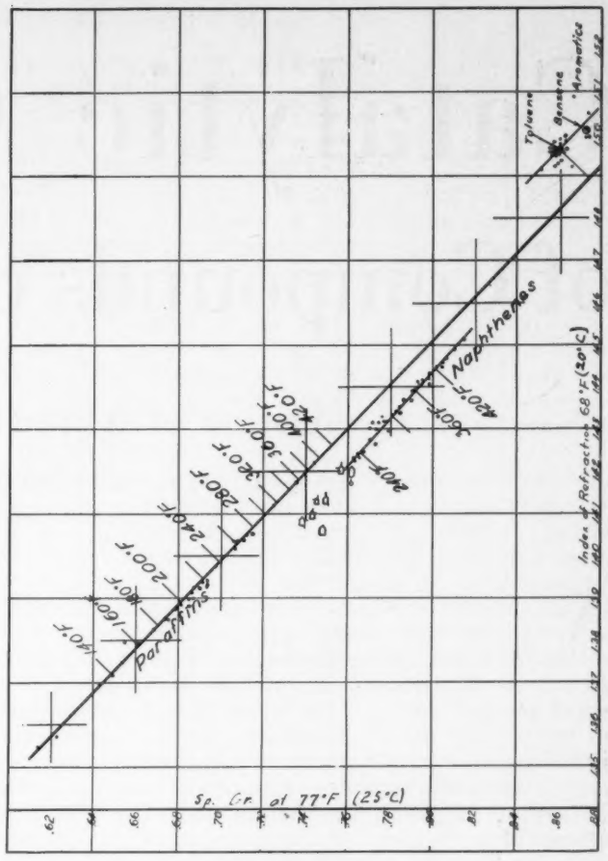

FIGURE 14
Specific gravity vs. index of refraction of saturated hydrocarbons.

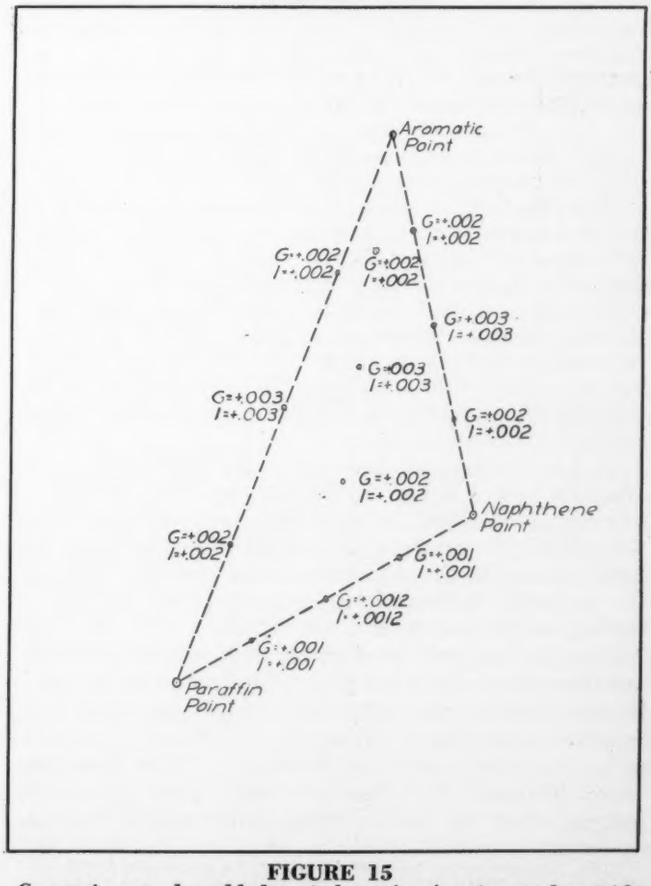

FIGURE 15
Corrections to be added to index of refraction and specific gravity at various points on graph of specific gravity vs. index of refraction.

Catalytic Cyclization of Compounds of the Fatty Series

I. Cyclization of Aliphatic Hydrocarbons by Means of Chromic Oxide

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ALL known methods of preparation of aromatic hydrocarbons from hydrocarbons of the fatty series are based on the thermal treatment of the latter. Processes of aromatization of this kind take place in vapor-phase cracking and pyrolysis at high temperatures of about 650-750° C. Paraffin hydrocarbons are subjected to reactions of decomposition, condensation and dehydrogenation, as a result of which aromatic hydrocarbons are formed. Transformations of this kind are connected with deep decomposition of the original molecule, and for this reason, the structure of the aromatic hydrocarbons obtained has no generic connection with the structure of the initial compounds. The present day hypotheses of the origin of aromatic hydrocarbons in pyrogenetic processes are based on the assumption that the aromatic hydrocarbons are formed at the expense of products of far-reaching decomposition of the initial hydrocarbons, for instance, butadiene, ethylene, etc. The theories of direct cyclization of long hydrocarbon chains have little following because of the absence of confirming experimental material.[1] In a study of isomerization of hydrocarbons of the fatty series in the presence of various catalysts, we succeeded in direct cyclization of aliphatic hydrocarbon chains.[2] It appears that fatty hydrocarbons containing 6 or more carbon atoms are converted, on being passed over amorphous chromic oxide at temperatures above 400°C., into corresponding aromatic hydrocarbons with the same number of carbon atoms as the initial hydrocarbon, with splitting off of hydrogen. This process has been called catalytic cyclization.

In this process, we observed in the liquid product no fractions boiling below the initial compound. The gases, however, contained, in addition to hydrogen, some saturated hydrocarbons. The boiling temperature of the liquid products of reaction was even increased because the aromatic hydrocarbons formed possessed higher boiling points than the initial aliphatic hydrocarbons. Normal octane gave good yields of o-xylene and small amounts of ethylbenzene. Normal heptane gave toluene, hexane gave benzene. Isoparaffins were also easily subjected to cyclization. Diisobutyl (2,5-dimethylhexane) gave, on being passed over chromic oxide, p-xylene while diisoamyl (2,7-dimethyloctane) gave m-cymene, judging from the boiling temperature of the reaction product and from isophthalic acid obtained from it on oxidation.

The reaction of cyclization over chromic oxide has been observed not only in the case of paraffin hydrocarbons, but in the case of compounds belonging to a different class as well—olefins and fatty aromatic compounds. The cyclization reaction goes on with special ease in the case of olefins. The octene gave o-xylene; cetene was converted into aromatic hydrocarbons, judging by the refractive index. Butylbenzene gave naphthalene. Cyclization of butylbenzene is more difficult than that of paraffin hydrocarbons and formation of larger quantities of saturated hydrocarbons is observed in the gases.

Thus, the reaction discovered by us is that of direct cyclization of long-chain hydrocarbons, the cyclization not being connected with original decomposition of the molecule, for the structure of the obtained aromatic hydrocarbon entirely depends upon the initial aliphatic hydrocarbon.

Besides aromatic hydrocarbons, the products of catalytic cyclization of paraffin hydrocarbons contain also a certain amount of olefins, the formation of which can be explained by dehydrogenation of initial hydrocarbons over chromic oxide—the reaction which was studied by Frey and Huppke for the case of lower paraffin hydrocarbons.[3]

In order to find out whether the action of chromic oxide is specific for the process discovered, we carried out experiments of catalytic cyclization of normal octane in the presence of other catalysts. These experiments

* This translation has been submitted by the Petroleum Division of the American Chemical Society. The Petroleum Division, however, assumes no responsibility for the facts and opinions presented in this paper, nor does it necessarily endorse statements made therein, nor does this publication.

show that catalytic cyclization of paraffin hydrocarbons goes on also under the influence of other dehydrogenating catalysts, such as, for instance, molybdenum disulfide or activated carbon. These results will be published in detail in the near future.

Experimental part: The experiments were carried out in a glass tube placed into an electrical tubular furnace. (Details of the set-up are given in our article in J. Gen. Chem. U.S.S.R. **7**, 131, 1937; Cf. Foreign Literature Service Abstract 11A.) The catalyst was prepared by reducing chromic anhydride with methyl alcohol in the presence of sulfuric acid and precipitating the obtained chromic sulfate with ammonia. The precipitated chromium hydroxide was carefully washed and dried at 100° C. The $Cr_2O_3.xH_2O$ was pressed using a pressure of 180-200 atm., then it was ground to a particle size of 2-4 mm. in diameter and dried in a furnace in a stream of hydrogen first at 150° C. and then at 450° C., at which temperature the catalyst was kept for several hours. The experiments were carried out using 40 gr. Cr_2O_3 occupying in the tube a space of 23 ml. The product was fed into the reaction tube from a special burette from which it was expelled by mercury dropping into it from a dropping funnel. The liquid products of the reaction were collected into a receiver, and the gases were led to a gasometer. In the products of reaction, the unsaturated hydrocarbons were determined by the bromide-bromate method and the aromatics by the difference between the amount of compounds sulfonated by 100 percent sulfuric acid (percent by weight) and the amount of unsaturated compounds calculated by the bromine number; the determination was checked by the specific gravity and the refractive index. The gas analysis was carried out by absorbing the olefins with bromine water, and oxidizing the hydrogen and the saturated hydrocarbons by combustion over cupric oxide.

Cyclization of normal octane. The normal octane prepared by the method of Wurtz from normal butyl bromide and sodium had a boiling point of 125-127° C., d_{17}, 0.704 and n(17/D), 1.3990. It was passed over chromic oxide with a velocity of 1 ml. per 10 minutes. The temperature was kept at 460° C. 480 ml. gas was evolved per each ml. of the substance passed. The gas contained 92.3 percent hydrogen, 7 percent saturated hydrocarbons and 0.7 percent unsaturated. The colorless product collected had d_{17}, 0.823 and n(17/D), 1.4660. It contained 6 percent unsaturated and 63 percent aromatic hydrocarbons. On distillation of the obtained products from a flask with a fir shaped dephlegmator, 24 percent boiled at 125-130° C. and 61 percent at 130-140° C.

To identify the aromatic hydrocarbons formed, a small sample of the product was oxidized with an alkaline solution of permanganate on a water bath. The acids formed by oxidation were treated with chloroform in order to separate the phthalic acids from the benzoic acid. The major part was insoluble in chloroform. The chloroform solution gave on distillation long needles of phthalic anhydride melting at 128° C. and giving a positive fluorescence test. The presence of o-xylene in the product was proved by preparation of tetrabromorthoxylene by the method of Gustavson. 0.3 ml. of the product was carefully added in drops to a test tube cooled with ice and containing 1.5 ml. bromine and a small amount of aluminum bromide made by addition to the bromine of a few milligrams of aluminum wire. After the reaction was completed, the bromide formed was washed with a dilute solution of ammonia and recrystallized from ligroin. A single recrystallization gave colorless silky needles melting at 259° C. Mixing a sample of this substance with tetrobromide made from synthetic o-xylene gave a melting point of 260° C. Consequently, the presence of o-xylene in the product can be regarded as established.

To study the mechanism of cyclization of normal octane, we carried out an additional series of experiments. These experiments aimed at clarification of the influence of the contact period upon the composition of the obtained products as well as of the question whether o-xylene is the only aromatic compound obtained in the process. For these experiments, normal octane was subjected to an additional treatment with antimony pentachloride in order to remove the isomers possibly present in small amounts. The results are given in Table 1.

Carrying out the entire series of experiments with the same amount of catalyst was difficult under the conditions of our set-up because of the necessity to vary the feeding rate in wide intervals, and for this reason the amount of catalyst was changed in some experiments. In experiments numbers 152, 153, 154, we used 45.5 g. chromic oxide, for experiment number 157, we used 35.7 g., while for experiment number 159, 23.8 g. For a comparison of the results of each experiment, we took into account the contact period, i.e., the period during which the product remained in the zone of the catalyst. To calculate the contact period, we recorded the amount of gas formed because the large amount of gas evolved in aromatization strongly changes the period during which the product remains in the zone of the catalyst. The results show that increasing the contact period brings about an increase of the amount of aromatic compounds in the product of reaction and a decrease of the amount of olefins. This is apparently explained by aromatization of the olefins themselves, after they are formed in the process of dehydrogenation; this was shown by us to be the case with octene, as reported below; in this way the olefins are removed from the reaction.

The amounts of naphthenes are shown in Table 1, determined by the aniline method after removing unsaturates and aromatic hydrocarbons and calculated by means of tables for the fractions 125-150° C.[4] They can be neglected and we can assume that these are practically absent in the products of aromatization, when the small values for the amounts as well as shortcomings in the exactness of the method itself are considered.

The data of Table 1 show that there is a big difference between the amount of substance passed and that of the obtained products. The gas analysis shows that these large losses cannot be explained by formation of gaseous hydrocarbons and are due, to a considerable extent, to carrying away a part of the reaction products by the large amount of gases formed. In addition, a certain quantity of the product is decomposed and remains on the catalyst in the form of tar which results in a decrease of the activity of the catalyst. A specially conducted experiment under conditions similar to those of experiment 1of Table 1 was aimed at accumulation of highly aromatized products and gave the following results: 21.5 ml. passed gave 10.8 ml. product and an increase of the weight of the catalyst by 1.2 g. This increase in the weight can be explained only by formation of high molecular non-volatile products because, after finishing each experiment, hydrogen was blown through the tube containing the catalyst.

The data of Table 1 are represented graphically in Figure 1. It is necessary to bear in mind that chromic

TABLE 1

Cyclization of normal octane over chromic oxide

CONDITIONS OF THE EXPERIMENTS						PRODUCTS OBTAINED IN THE EXPERIMENTS								
						Liquid Products					Gases			
								Comp. Percent by Weight						
Experiment No.	Temp. of the Experiment °C.	Time of Feeding of 1 Ml. Octane Min.	Contact Period, Min.	Ml. Octane Passed	Ml. Product Obtained	d_{17}	$n_{17/D}$	Unsat.	Arom.	Naph.	Ml. Gas per 1 Ml. Oct. Passed	$C_n H_{2n}/2$	$C_n H_{2n}$	H_2
152	460	13.1	0.5	18.0	6.5	0.861	1.4955	3	94	2	650	7.0	0.8	92.7
153	460	6.4	0.3	18.0	8.2	0.817	1.4705	5	72	2.5	454	7.4	0.6	92.0
154	460	3.1	0.17	14.0	5.0	0.797	1.4540	8	56	4.5	335	6.9	0.3	92.8
157	459	3.5	0.14	14.0	6.4	0.779	1.4422	8.5	45	3	225	Not analyzed		
159	459	2.1	0.08	.....	...	0.742	1.4200	10	21	3	Not deter'd			

oxide loses its activity in the course of the experiments and for that reason the last experiments, having low contact periods, gave somewhat lower values.

The highly aromatized product collected from two experiments, carried out similarly to number 1 of Table 1, was subjected to an investigation in order to find out whether the o-xylene is the only product of aromatization of normal octane. The product was subjected to two fractionations, using a small flask with a dephlegmator. The results are as follows:

Boiling starts	127°
127-130° C.	4.9 percent
130-135° C.	11.2 percent
135-137° C.	14.0 percent
137-140° C.	46.9 percent
140-141.5° C.	16.8 percent
Residue and losses	6.2 percent

As seen from these data, the products of reaction contain no low-boiling fractions in spite of the almost complete conversion of normal octane into aromatic hydrocarbons. The bulk of the product, 77 percent, boils within 135-141.5° C. The fraction 140-141.5 percent had a refractive index n(20/D), 1.5028. The fractions boiling 130-140° C. were investigated because we thought that in addition to o-xylene, they might contain ethyl-benzene, the formation of which could be expected to go on simultaneously with o-xylene according to the scheme $CH_3 (CH_2)_6 CH_3 - - C_6H_5.O_2H_5$ (or $CH_3 . C_6H_4 . CH_3$) $+ 4H_2$.

The combined fractions boiling at 130-140° C. had an n(20/D), 1.4960. This was oxidized with potassium permanganate. 4.25 g. of the product were put into a round bottom flask fitted with a mercury seal, a stirrer and condenser. 500 ml. water, 6 ml. 30 percent sodium hydroxide and some potassium permanganate were added. The flask was heated on a water bath for 8 hours with stirring. Additional potassium permanganate was added when the previous portion was discolored; 15 g. potassium permanganate in total were used. After the oxidation was finished, the solution was discolored with methyl alcohol, reduced in volume in a porcelain dish on the water bath and acidified with hydrochloric acid. The precipitated acids were filtered and washed with water on the filters, those remaining in the mother liquor were extracted with ether, and the ether solution evaporated leaving the acids behind. A total of 3.14 g. acids was obtained. To isolate the benzoic acid, the raw acids were treated with chloroform in the cold. The product soluble in chloroform amounted to 0.58 g., that insoluble in chloroform, to 2.5 g. The soluble acids were recrystallized from 11 ml. boiling water in the presence of activated carbon. 0.16 g. benzoic acid melting at 121.5°C. were obtained. A mixed test with pure benzoic acid showed no change in melting point. The benzoic acid was titrated with sodium hydroxide and consumed the theoretical quantity of it. The acids insoluble in chloroform were recrystallized from 12 ml. boiling water, a part of the acid remaining insoluble. The volume of water used for recrystallization was calculated, taking into account the solubility of o-phthalic acid. On cooling, there crystallized out of the water 1.56 g. o-phthalic acid, which melted in a sealed capillary at about 190° C. and on distillation gave phthalic anhydride melting at 130° C. The theoretical quantity of sodium hydroxide was consumed in titration of a sample of this phthalic acid. The acids remaining insoluble in the recrystallization of o-phthalic acid were again treated with boiling water; 0.05 g. remained insoluble (acid A) and the part that dissolved crystallized out in the amount of 0.047 g. (acid B). Both acids (A and B) sublimed at about 300° C.

Both acids were converted into methyl esters. For this purpose, each acid was sealed into a small glass tube with 1 ml. methyl alcohol and 2 drops of concentrated sulfuric acid and heated on a water bath for 6 hours. On cooling, nothing separated in the tube with acid B, while in the tube containing acid A, ester crystallized out in the form of mother of pearl leaves. The contents of each tube were treated with a solution of soda and extracted with ether. After evaporation of the ether, the methyl ester was obtained from the acid B, and this showed after distillation a melting point of 63-64°; the melting point remained unchanged on repeated distillation. Consequently, judging from the melting point, we obtained the dimethyl ester of m-phthalic acid. In a similar way, from the acid A, an ester was prepared in the amount of 0.03 g., and this possessed a melting point of 139° C. A mixed sample with dimethyl ester of p-phthalic acid melted at 139-140° C. Thus, from 3.14 g. of raw acids (the value corrected for the loss of benzoic acid and o-phthalic acid in recrystallization) we obtained:

Benzoic acid	0.2 g.	6.3 percent
o-phthalic acid	1.65 g.	52.4 percent
m-phthalic acid	0.047 g.	1.6 percent
p-phthalic acid	0.05 g.	1.8 percent

Assuming that these proportions of acids obtained hold true also for the corresponding aromatic hydrocarbons, we obtain the following composition for the aromatic hydrocarbon mixture resulting from cyclization of normal octane:

o-xylene	about 85 percent
ethyl-benzene	about 10 percent
m-xylene	2.5 percent
p-xylene	3 percent

The amount of o-xylene obtained in this calculation is somewhat reduced at the expense of other hydrocarbons because, according to M. Nemtsov and F. Shenderovich[5] oxidation of o-xylene with permanganate results in formation of o-phthalic acid which is oxidized

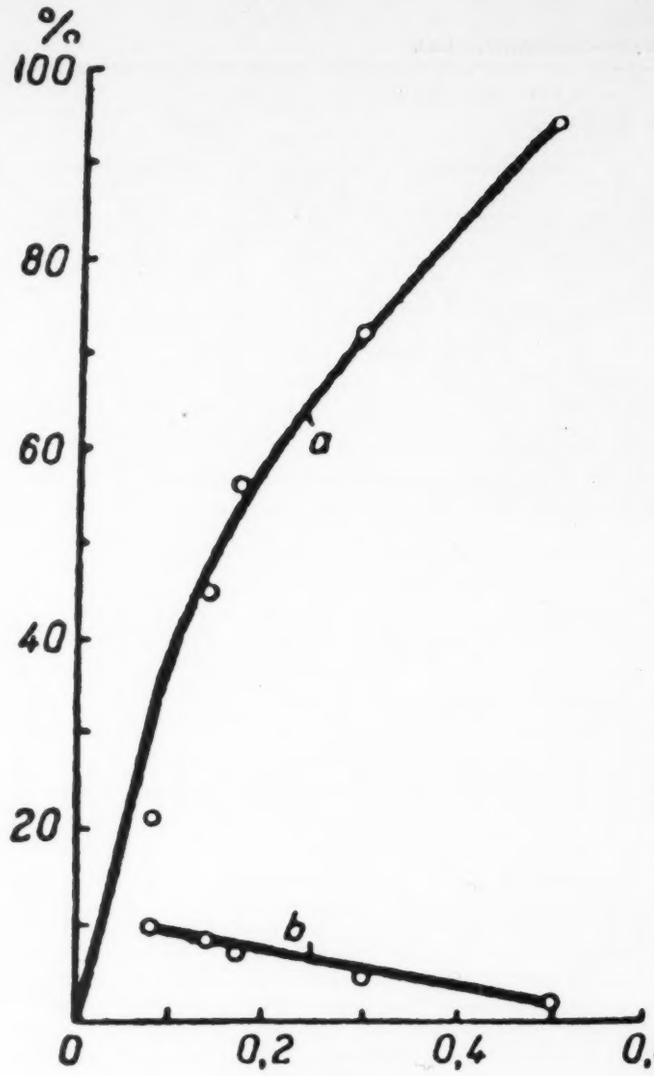

FIGURE 1
Contact Period.

with much more ease than the benzoic acid formed from ethylbenzene and also apparently more easily than m- and p-phthalic acids; for this reason, the products of oxidation are enriched with benzoic, m- and p-phthalic acids at the expense of o-phthalic acid. Summarizing the results of the analyses of the products of aromatization of normal octane, we can see that the basic product of aromatization is o-xylene and the cyclization reaction with formation of ethyl-ebnzene goes on with considerable difficulty. This is apparently explained by the fact that secondary carbon atoms are more easily dehydrogenated than primary carbon atoms. The origin of m- and p-xylene, the presence of which is established by formation of the corresponding phthalic acids, can be explained in two ways: (1) by isomerization of o-xylene or ethylbenzene in the process of the experiment similarly, for instance, to isomerization of p-xylene into m-xylene which was observed in pyrolysis by G. Baddeley and J. Kenner[6], or (2) by isomerization of the initial normal octane followed by cyclization of the isomers resulting from it.

Cyclization of normal heptane. Normal heptane prepared by reducing dipropyl ketone, melting at 96-98°C. and having a d_{17}, 0.684 and n(17/D), 1.3865 was passed with a velocity of 1 ml. per 10 minutes over chromic oxide at 470° C., 270 ml. gas were evolved per 1 ml. heptane passed; the gas contained 94.2 percent hydrogen and 5.8 percent saturated hydrocarbons. The liquid product possessed a d_{17}, 0.740 and n(17/D), 1.4196 and boiled at 98-103° C. It contained 8 percent unsaturated and 26 percent aromatic hydrocarbons. For the purpose of identification of the aromatic hydrocarbons formed, the product was nitrated. This was done by treatment of 1 ml. of the product with 3 ml. of sulfuric acid (1.84) and addition of 5 ml. nitric acid (sp. gr. 1.50) to the solution. After completion of the reaction, the product was heated on a water bath, poured into water and extracted with ether. Two recrystallizations from alcohol gave 2,4-dinitrotoluene melting at 69.5° C.

Cyclization of normal hexane. Normal hexane prepared from propyl bromide and sodium, boiling at 69-70° C. and possessing a d_{17}, 0.660 and n(17/D), 1.3755 was passed with a velocity of 1 ml. per 10 minutes over chromic oxide at 470° C. 130 ml. gas were evolved per 1 ml. of hexane passed. The liquid product possessed a d_{17}, 0.695 and an n(17/D), 1.3965; it contained 10 percent unsaturated and 17 percent aromatic hydrocarbons. The presence of benzene in the product was proved by nitration similarly to the product obtained from heptane. The 1,3-dinitrobenzene obtained melted at 90° C.

Cyclization of diisobutyl (2,5-dimethylhexane). Diisobutyl was prepared from isobutyl bromide and sodium and boiled at 105-109° C., possessing a sp. gr. of 0.693 and an n(17/D), 1.3955. It was passed over chromic oxide at 464° C. with a velocity of 1 ml. per 8 minutes. 286 ml. gas were evolved per each ml. of the product passed; the gas contained 85 percent hydrogen and 15 percent saturated hydrocarbons. The obtained product possessed a sp. gr. 0.759, an n(17/D), 1.4315 and contained 10 percent unsaturated and 36 percent aromatic hydrocarbons. A fractional distillation resulted in 58 percent distilling at 107-120° C. and 33 percent at 120-140° C. The identification of aromatic hydrocarbons was carried out by oxidation of a sample of the product with permanganate in alkaline solution. The product obtained was almost insoluble in chloroform, alcohol or ether and distilled above 300° without decomposition. It was converted into methyl ester by heating for 8 hours on the water bath in a small sealed tube with 5 parts of methyl alcohol and one part of sulfuric acid of a sp. gr. 1.84. The obtained colorless plates of dimethyl ester of terephthalic acid melted at 139° C. Consequently, the presence of p-xylene in the product of cyclization of diisobutyl can be regarded as proved.

Cyclization of diisoamyl (2,7-dimethyloctane). Diisoamyl was prepared from isoamyl bromide and sodium by the Wurtz method. It boiled at 159° C., had a sp. gr. 0.726 and n(17/D), 1.4115. It was passed over chromic oxide with a velocity of 1 ml. per 10-12 minutes at 458°C. Each ml. of the product passed evolved 490 ml. gas containing 90.3 percent hydrogen and 9.7 percent saturated hydrocarbons. The obtained product possessed an n(17/D), 1.4861 and a sp. gr. d_{17}, 0.844. It contained 9 percent unsaturated and 82 percent aromatic hydrocarbons. After two fractionations, the following results were obtained.

Up to 155° C.	9.9 percent
155-165° C.	15.8 percent
165-178° C.	70.4 percent

The fraction 165-178° C. was oxidized with potassium permanganate under the same conditions as those used in the case of octane. The acid obtained from the oxidation was sparingly soluble in water and gave a readily soluble barium salt (which is characteristic for

TABLE 2
Cyclization of Aliphatic Hydrocarbons over Cr_2O_3

Experiment No.	Hydrocarbon	Temperature of Experiment °C.	Period of Feeding of 1 Ml. Hydrocarbon, Min.	Boiling Range °C.	REACTION PRODUCTS: LIQUID PRODUCTS: d_{17}	$n^{17}D$	Composition, Percent by Weight: Olefins	Aromatics	Aromatic Hydrocarbons: Hydrocarbons	Identified as	GASES: Amount of Gas Evolved per 1 Ml. of Substance Passed, Ml.	Composition, Percent by Volume: H_2	C_nH_{2n}	C_nH_{2n+2}
92	Normal Octane	460	— 10	125–127 125–140	0.704 0.823	1.3990 1.4660	— 6	— 63	— o-Xylene	— (1) o-Phthalic Anhydride, M. P. 129° C. (2) Tetrabromo-xylene, M. P. 259° C.	— 480	— 92.3	— 0.7	— 7.0
95	Normal Heptane	470	— —	96–98 98–103	0.684 0.740	1.3865 1.4196	— 8	— 26	— Toluene	— 2, 4-Dinitrotoluene, M. P. 70° C.	— 270	— 94.2	— —	— 5.8
97	Normal Hexane	470	— 10	69–70 —	0.660 0.695	1.3755 1.3965	— 10	— 17	— Benzene	— 1, 3-Dinitrobenzene	— 130	— 76.3	— 0.5	— 23.2
98	Diisobutyl	464	— 8	105–109 107–140	0.693 0.759	1.3955 1.4315	— 10	— 36	— Paraxylene	— Dimethyl Ester of Terephthalic acid, M. P. 139° C.	— 286	— 85.0	— —	— 15.0
99	Octene, Mixture of 1 and 2	460	— 6	122–126 127–136	0.724 0.783	1.4105 1.4470	— 49	— 43	— o-Xylene	— o-Phthalic Anhydride, M. P. 129° C.	— 200	— 89.0	— —	— 11.0
166	Diisoamyl	458	— 10–12	158–159 155–178	0.726 0.844	1.4115 1.4861	— 9	— 82	— m-Methylisopropylbenzene	— Dimethyl ester of m-Phthalic ester, M. P. 64° C.	— 490	— 90.3	— —	— 9.7
130	Butylbenzene	472	— 10	181.5–183.5 —	0.862 —	1.4920 —	— 12	— 12*	— Naphthalene	— Naphthalene Picrate	— 580	— 74.2	— —	— 25.8
134	Cetene	450	— 10	— —	— —	1.4430 1.5250	— —	— —	— —	— —	— 600	— 91.5	— —	— 8.4

* Percent of Naphthalene determined by the Picrate method.

m-phthalic acid). For purification the barium salt was decomposed with hydrochloric acid, and the liberated acid recrystallized from a large amount of boiling water. The acid was then converted into the dimethyl ester by heating for 8 hours with methyl alcohol and sulfuric acid in a sealed tube on the water bath. The ester had a melting point of 64° C. Thus, the presence of m-phthalic acid should be regarded as proved. The aromatic compound obtained was apparently m-methyl-isopropylbenzene which is confirmed by formation of the m-phthalic acid.

Cyclization of octene. The mixture of octene-1 and octene-2 prepared by dehydration of octanol-2 had a boiling point 122-128° C., d_{17}, 0.724 and n(17/D), 1.4115. It was passed over chromic oxide at 460° C. with a velocity of 1 ml. per 6 minutes. About 200 ml. gas were evolved per each ml. octene passed, and this contained 8.9 percent unsaturated and 11.0 percent saturated hydrocarbons. The obtained product possessed a d_{17}, 0.783 and n(17/D), 1.4470. 50 percent of it distilled at 127-130° C. and 48 percent at 130-136° C. It contained 49 percent unsaturated and 43 percent aromatic hydrocarbons. Oxidation with permanganate in alkaline solution followed by distillation gave phthalic anhydride melting at 129° C.

Cyclization of butyl benzene. Butyl benzene boiling at 181.5-183.5° C. was passed over chromic oxide at 472° C. with a velocity of 1 ml. per 10 minutes. Each ml. of butyl benzene passed evolved 580 ml. gas consisting of 74.2 percent hydrogen and 25.8 percent saturated hydrocarbons. The product obtained contained 12 percent unsaturated and 12 percent naphthalene determined by the picrate method.

SUMMARY

Table 2 gives a general summary of the results obtained with individual hydrocarbons, with the exception of those experiments which are given in Table 1. Experiments 92-98 were carried out using the same catalyst. The results show that a decrease in the molecular weight of the hydrocarbon reduces the velocity of its aromatization (compare the experiments 92, 95 and 97). The percent of aromatic hydrocarbons in the latter case is lower, even though a higher temperature is used in the experiment. The lowering of the percentage of aromatic hydrocarbons is caused in these experiments to some extent also by the reduced activity of the catalyst; however, a comparison of the experiments 97-98 shows that this cannot be the only cause of the decrease in percentage of the aromatic hydrocarbons, for a change to a compound with a higher molecular weight (diisobutyl), brings about a new increase in the percent of conversion. In the same way, the experiment with diisoamyl, carried out with fresh catalyst, shows a higher percentage of conversion than experiment 92 carried out with normal octane using the same amount of fresh catalyst.

The summary given in Table 2 accounts also for experiment 134 carried out with cetene which has not been mentioned in the text. We had at our disposal only a small amount of cetene, and the product obtained in this experiment was not analyzed. Only the refractive index was determined, and this showed that the product was completely aromatized.

The investigation of the process of catalytic cyclization is being continued. The chemists, S. Livshits and S. Vainshtein, participated in carrying out separate experiments.

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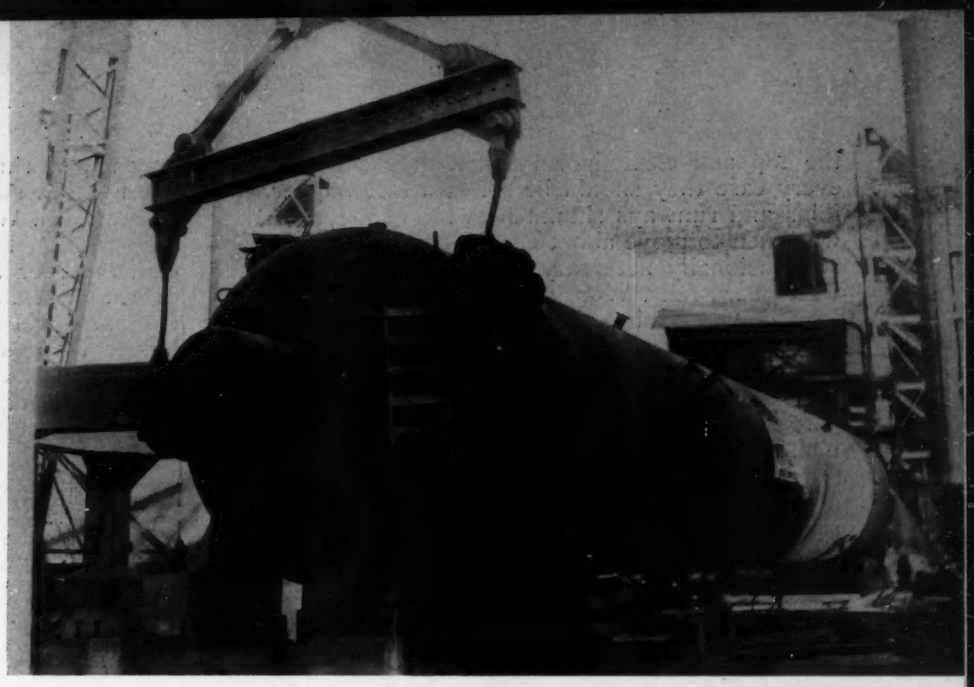

Use of lifting lugs or cars for raising heavy towers.

Safety in the Design, Construction and Maintenance of Combination Cracking Units

PART 2

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M. W. Kellogg Company

SAFETY IN CONSTRUCTION

WITH the completion of design comes construction. At the outset it is to be emphasized that safety in construction starts with the attitude of the superintendent of construction and his assistants. The habit of care and the habit of correct working procedure can be inculcated, and it is with the supervisors that these habits must be started. This means that those in charge of construction must know the rules of safety and that they must enforce them. By their precepts and examples they can and should keep their workmen constantly impressed with the need of proper action during construction. Obviously, a body of men regularly engaged in construction can be more easily kept in a responsive attitude toward safety regulations than occasional workers. Nevertheless, it is advisable that the principles of safe work be constantly called to attention, and that means be provided to enable men to apply what they know about safety.

All tools should receive regular inspection and be kept in good condition. Defective tools create a variety of risks. A hammer loosely held on its handle, or one having a split handle, may fly off and injure a man. A hammer or chisel with a badly mushroomed head may cause metal slivers to fly into an eye unprotected by goggles. A wrench with jaws in poor condition may slip and fracture a knee. Faults of a serious nature in hand tools and power tools should be promptly repaired or the tools should be rejected.

Safe tools are not enough. It is necessary that workmen use them in a safe manner. Numerous tools require a certain technique in use. Tools may be incorrectly used, or the wrong tool may be employed for a given job. There are many dos and dont's with which a well qualified foreman is familiar. These should be taught and observed. A competent, watchful foreman can do much toward the completion of a piece of work without an accident. This fact is to be emphasized.

Temporary structures erected in the course of construction of equipment should be set up in accordance with certain rules of safety. Ladders should be soundly built, sufficiently long and set firmly in place. It is often necessary that they be lashed in place at

* Presented before the annual meeting, Petroleum Division, National Safety Council, Chicago, October, 1938.

the top and cleated or blocked at the bottom. In every case they should be set at a safe angle. Scaffolds and runways should be wide enough to allow workmen to move about easily without crowding. It is occasionally necessary that scaffolds be provided with guard rails. Workmen may be inclined to jump from one scaffold to another or from a scaffold to the ground. This is bad practice if the scaffolds are an appreciable distance from the earth. Scaffolds should not be dismantled or moved unless all loose material is removed from them. This is a precaution to protect men below from falling objects. Floor openings in temporary structures should be covered, except when in use, by gratings or cleated covers or enclosed by rails, so that men will not accidentally step into them and fall through. Nails are a fertile source of accidents.

The conveyance of structural materials offers a good field for the exercise of safety rules. In lifting and carrying objects by hand, workmen should be careful not to injure themselves by adopting faulty postures. Ruptures may easily result from an incorrect manner of lifting. Heavy objects have a safe and an unsafe way of being handled. Men should learn and pursue the proper procedure. Furthermore, loads that are too much for one man should always be handled by the correct number.

A little ingenuity can greatly assist in working the transportation of materials by hand more safely. For instance, at the cost of a few dollars, a carrier or cradle can be constructed for transporting by hand cylinders for compressed gases, such as acetylene. The chance of slipping of these heavy objects is eliminated, and only two men ordinarily are needed to carry them. Heavy pipe and bars can be safely carried in lengths of chain suspended from strong cross bars held at each end by a man. Carriers for handling floor plates can be devised in a similar manner.

HOISTING MACHINERY

When hoisting machinery is being used, it is good policy to test brakes and other controls at the start of each working shift. This also applies to such hoisting equipment as cable guides, chain falls, rope and wire slings and shackles. Hoisting engines preferably should have housings, where the operator may stand without the risk of being hit by falling objects or by the backlash of a breaking cable. It is necessary that operators of hoisting equipment know the allowable loads that can be carried and that they refrain from lifting or moving greater loads.

Loading and unloading equipment for transferring objects into and out of cars or trucks, should be firmly set in position to avoid slipping. Vehicles should be fixed in place, for otherwise they may move sufficiently to cause material to fall or slide upon a workman. Loading platforms and runways require adequate width and firm construction. In the hoisting of small objects during construction tubs and buckets are commonly used. These should have their bails strongly attached and should possess good bottoms to avoid spilling their contents upon men below. Men should not stand beneath materials being hoisted. This is as true in the case of small objects as it is for girders and plates.

"Good housekeeping" helps promote safety during construction. Good housekeeping means orderliness. This is possible even in the midst of a busy scene. There is no need to keep tools or material for which there is no current demand lying around where they may trip workmen or fall upon them. It is bad practice to allow such objects to lie in walkways or loose on scaffolds. Where possible, timbers and other long objects should be stored horizontally rather than on end, in order to reduce the danger of their falling over. Scraps and debris should be promptly removed from places of work. Oil pools should not be tolerated longer than is necessary where men are working, because a man may easily slip in them and because there is chance of an accidental fire starting in the oil.

Workmen should exercise caution when doing work near equipment in operation. This is particularly applicable to work involving welding, metal chipping or grinding when done in situations where sparks may be generated in the presence of inflammable vapors or light oils. It is often necessary to use electric lights on extension cords when performing some work. Cords should be kept in good condition to avoid sparks from broken connections. Wire guards are always necessary on light bulbs to prevent breakage.

Proper attire for workmen can promote safety during construction. Shoes with sound soles and well protected toes help to avoid foot injuries. Construction workers are often required to wear safety helmets. They may prevent the fracture of a skull by falling objects. The importance of goggles for protecting the eyes is widely recognized. Welding, torch cutting, grinding, chipping, drilling and riveting create hazards that can be minimized by the use of goggles designed for the purpose.

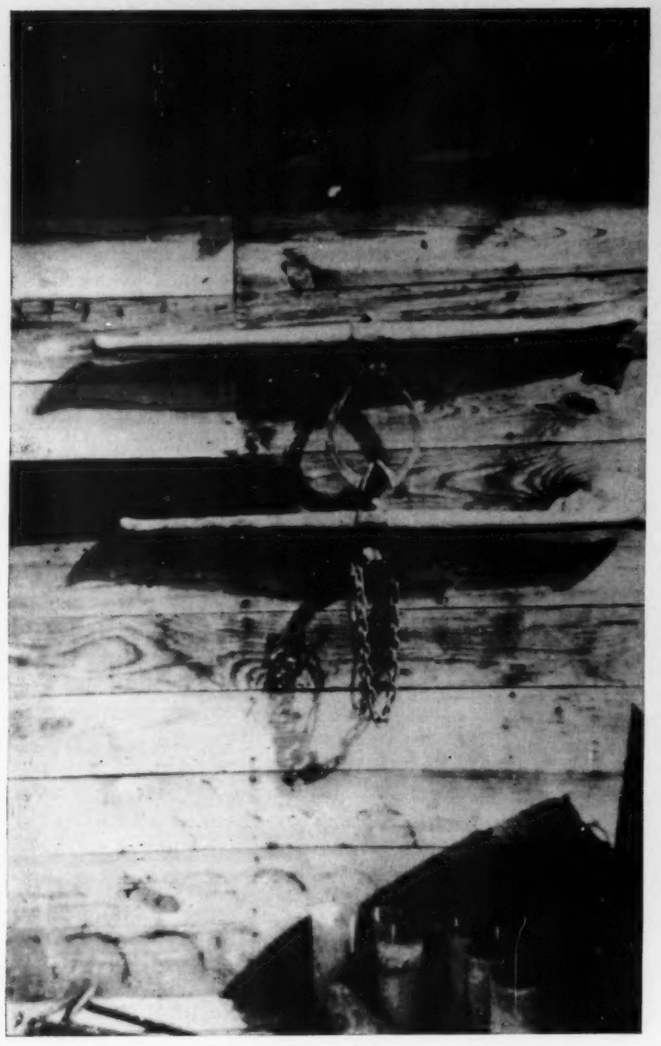
Men working above other workmen can often be provided with means of reducing the danger of dropping tools. In some instances it may be possible and advisable to attach their tools to themselves. For instance, it has been found practicable and efficacious to attach sash cords to the base of the handles of spud wrenches. These cords are fastened to the workmen's belts, and are sufficiently long to allow easy use of the tools. This idea is applicable to tools of many types.

The foregoing are probably the main points to observe in the maintenance of safety during construction. They do not exhaust the subject. Many jobs present their own peculiar problems, but in the main what has been said applies to most work. Adherence to safety rules is the best assurance against damage to equipment and injury to men. It is obvious that all injuries, whether serious or minor, should be promptly reported to the foreman or superintendent so that adequate first-aid and necessary subsequent treatment may be provided; to this there should be no exceptions.

MAINTENANCE

The principal means of promoting safety in the operation of a combination unit is inspection. Even the best designed equipment ages and suffers the attacks to which refinery installations are subject. Some of these attacks are negligible and apparent at a casual glance. Others, however, corrosion among the worst, are matters of great concern. They occur often out of sight and in more or less inaccessible places. If allowed to continue long enough, these ravages may progress to the point where further operation is dangerous. Careful inspection is imperative, particularly for operations at high temperature and pressure. Probably the best results can be obtained by a regular refinery inspection group in charge of an engineer and kept informed on recent developments

Pipe carriers are easily made and cheap, and in use they give equal distribution of the load.



in methods of inspection. Each inspector is an expert in his line. Specialization makes for a high degree of competence in inspection. This is very necessary in the case of the inspection of instruments, which are generally too complicated to be entrusted to the care of anyone but a specialist. In the smaller plants a specialized group of inspectors may be impracticable. Nevertheless, systematic inspection is a necessary part of any safety program. Without this, safe maintenance of equipment is impossible.

A capable and vigilant inspector is essential in the pursuance of a good safety policy. This kind of inspector is one who is not afraid to get dirty. He is unwilling to take a second hand report of the condition of equipment from a workman who is not an inspector merely for the sake of saving his clothing. He is always anxious to learn about the condition of equipment by seeing for himself. For instance, he likes to examine the condition of piping and tubing by cutting the material open after it has been discarded. Naturally, the inspector deserves and must have the confidence and cooperation of the management and the workers in the plant. This is the assistance the inspector requires to perform his work most successfully.

Where may an inspector look for weaknesses in equipment? As a rule experience answers this question to a certain extent. Corrosion has been found generally most severe in towers opposite the points of entry of vapors. Nipples and sharp bends in piping also receive heavy attacks from corrosive, as well as erosive, action. Incidentally, some refineries make a practice of replacing all nipples once a year. Nipples are cheap, and to reject them periodically is a good precaution against failure. It has also been observed that piping is very susceptible to corrosion and erosion at the points of entry of fluids into the piping. However, the vigilant inspector will not restrict his examinations to these portions of equipment where weaknesses have developed in the past. Corrosion is by no means always predictable. The running of a different kind of crude from that customarily run on a combination unit may result in the appearance of corrosion at points where corrosion had not hitherto appeared. Also, a change in operating conditions from those ordinarily employed may accelerate corrosion. The same is true where there has been a change of metal parts used in equipment. In other words the sound attitude for an inspector to adopt is that corrosion as well as other weaknesses may be found anywhere until it is certain they are absent. From the foregoing considerations, it is apparent that the inspector should keep posted on any changes in the customary operation of a combination unit.

Policies regarding the frequency of inspections vary considerably. Some refineries make complete

inspections of all parts of equipment once or twice a year, regardless of whether the equipment or some portion of it has been idle part of the time. Others do not make these general inspections but frequently inspect their equipment at points where weaknesses are most likely to occur. Whether or not annual or semi-annual general inspections are made, it is advisable that the examinations of equipment subjected to severe conditions be made whenever equipment or a portion of it is idle. Only in this manner can current information on the condition of equipment be secured.

One subject with which inspection must concern itself is the weakening of metal walls by corrosion or erosion. Where adequate protection is not secured by specifying corrosion-resistant alloys, neutralizing chemicals such as lime, caustic or ammonia are often injected into vapor or liquid streams. Neutralizers have their individual defects and virtues. Whether a given chemical will be satisfactory in a particular situation must depend on its effectiveness as a neutralizer, its cost, its effect upon refinery products, its tendency to clog equipment and its bad influence, if any, on metals. Regardless of whether neutralizers are used, however, it is poor policy to dispense with inspection. Various devices for inspection are used. One is that of hammering piping and walls of vessels to detect thin spots. The hammering method is dependable only when employed by an experienced inspector. He locates thin areas in metal walls by noting a change in the pitch of the sound made by a hammer blow on the metal when a thin spot is struck. The hammer test should be supplemented by other inspection methods and not depended upon to the exclusion of other means.

One of the routine examinations made of equipment on combination units consists of inspection of the inside diameters of furnace tubes. Piping used for some services, particularly where very corrosive fluids are being handled, is also inspected in this manner. When the internal diameters of tubes and piping have become enlarged beyond a certain point determined by experience and the knowledge of metal strengths the equipment is no longer considered safe. A frequently adopted method of inspecting internal diameters is the use of inside calipers. These are so constructed as to obtain dimensions at considerable distance from the end of a tube or pipe. Another means of keeping check on the rate of thinning of a tube or pipe wall is the drilling of small test holes into the metal to within a distance of the inner wall equal to the corrosion allowance for the wall thickness. When the wall has thinned to the extent of destroying the corrosion allowance the fact is signified by development of a leak in the test hole. This method of inspection has its drawbacks. When surfaces are covered by insulation a leak occurring beneath insulation may not become apparent for some time. However, this drawback can be eliminated by welding over the drill hole a nipple that extends through the insulation. Leakage through small test holes of material that cokes easily may quickly be stopped by plugging, the purpose of the hole thus being defeated. Finally the use of test holes on vapor lines may be unsatisfactory by reason of immediate evaporation of the material; a visible indication of a leak is thus prevented. A variation of the test-hole method for keeping check on metal wall thicknesses consists of a hole sealed with a screwed plug. The plug may be removed periodically to allow entry of a caliper into the hole.

The use of test or sentry holes as described above is not confined to tubing and pipes. Such holes have been used in the walls of vessels. An often used means of determining the rate of thinning of vessel walls when the drilling of holes is undesirable consists in the welding of corrosion-resistant metal plugs or bench marks to the inner walls of vessels. The rate of corrosion is determined by periodic measurements of the distances from the top of the plugs to the face of the surrounding metal. These plugs have the advantage over drilled holes of not weakening the metal to which they are attached.

The inspection of joints is a necessary part of the safe maintenance of equipment. Joints subjected to stresses or exposed to high temperature or corrosive materials should have periodic examination. Welds and screwed and riveted joints receive regular inspections by careful refiners, and even those hidden beneath insulation are examined once or twice a year. Vessels having undergone extensive repairs are filled with water under pressure. Leaking joints are thus readily discovered. The application of the hydrostatic pressure test to piping is also practicable.

Safety valves, wherever used, require frequent inspection. They are generally examined whenever the vessels to which they are attached are not in use. In some plants the valves are removed from service after being replaced by spare valves and are given a thorough cleaning and testing. If not thus taken out of operation the valves should, nevertheless, receive such attention as can be given them. To receive the best possible attention a safety valve should be freed of coke or tarry matter, have its seat ground or polished and be tested for correct popping pressure.

INSTRUMENTS

Instruments are themselves inspectors, and to keep them in good working order is one of the duties of the instrument department. Any experienced instrument inspector knows that instruments may become unreliable from a number of causes. Piping to pressure gauges may become plugged. Pyrometer wires may develop poor connections. Floats that actuate liquid-level indicators or controls may leak. The mechanisms in automatic regulators may become faulty to the extent that the instruments fail to respond promptly enough to changes in temperature, pressure, liquid level or fluid flow. Cold weather may put instruments temporarily out of commission. Such contingencies mean that instruments require regular inspections to enable them to perform their important duty as watchdogs.

It ought to be obvious that inspection can render full value as a means of safety insurance only if full records are kept and studied. The men who make inspections in the field may or may not attend to the recording and analysis of the data they collect, but this office work has to be done. A comparison of periodic inspection data shows rates at which the walls of tubes, pipes and vessels are being thinned. It permits an estimate of the date at which equipment will have to be replaced or repaired. It reveals whether materials and types of equipment are suitable for the service for which they are being used. Properly interpreted, inspection data can be a reliable

diagnostician and guardian of the health of refining equipment.

Most of the points on safety brought out in the discussion of construction work apply equally well to repair work on a unit. Maintenance crews are essentially construction crews and are subject to much the same hazards as are present during construction. Safe practice in construction is generally safe practice in maintenance. However, there are risks in maintenance that are not usually encountered during new work. These risks arise from the fact that frequently during maintenance workmen must come into contact with petroleum liquids and vapors that were not present when a combination unit was built.

It is often necessary to enter and make repairs in vessels which have recently contained liquids or vapors. The vessels should be cleaned as thoroughly as possible before being entered. Otherwise there is danger that men may slip and fall, start fires or cause explosion with welding or cutting equipment. Petroleum vapors are dangerous not only because of the fire risk but also because of the possibility they may cause asphyxiation. Flushing with water or steaming out is usually successful in getting rid of accumulation of liquid. Gases may be removed from vessels by the use of steam jets discharging through open manholes or by a thorough steaming out. Men should never enter a vessel that has contained vapors until tests have shown the vessel to be free of vapors. All connections should be blanked off to keep vapors out during work. Steam lines should also be blanked off.

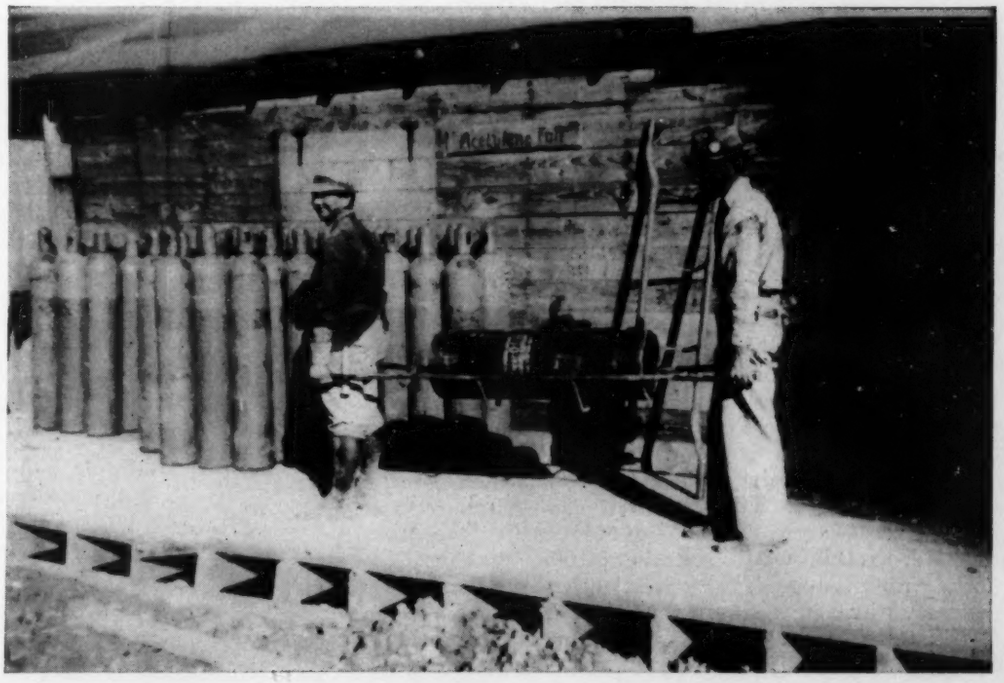
Furnace fire boxes should be entered with caution. Leaking oil burners may have created pools of oil that might be ignited by flames or sparks. Leaking fuel gas piping may have filled the fire box with gas after the furnace was removed from operation. Precaution should be taken to stop all leaks of fuel into the fire box. A safe practice is to insert blanks into the fuel lines before repair work is begun, not depending solely on block valves. A valve that may not be leaking sufficiently during operation to give trouble may allow enough inflammable material to pass through during repair work to cause an accident.

The repair and cleaning of piping that has recently contained oil or vapor calls for the application of safety rules. Piping may be cleaned in much the same way as vessels, and should be cleaned if there is chance of a fire or an explosion from open flames or sparks. It is advisable to close off a section of a line being repaired by insertion of a blind, or plate, into the nearest flange. A colored tag or other means of identification should be attached to the plate, so as to insure removal of the plate on completion of repairs.

Where men are at work in contact with equipment from which they might receive an electrical shock, the safe practice is to lock switches open, thus insuring that current will not be inadvertently switched into the equipment. In some situations, it is similarly advisable to lock valves which have been closed to prevent liquids and vapors from being blown upon men engaged in repair work.

Modern engineering and research have attained high efficiency in the design and construction of refining equipment. Operation at pressures and temperatures unfamiliar to the oil industry ten years ago can be made safe from the mechanical standpoint. Combination units embodying extreme operating conditions are capable of careful control. When properly designed and constructed to meet all conditions that may be anticipated they are as safe as present-day knowledge can make them.

After completion of construction it is necessary to put the equipment into operation. At this point enters the human element. Combination units, like individual distillation or cracking units, are not foolproof. They may approach mechanical perfection, but mechanical perfection is not proof against poor maintenance and errors in operation. After the engineer has performed his duty in the construction of a safe unit, it is then up to the refiner to provide well qualified operators and to keep the equipment in first-class operating condition. The human element cannot be ignored in a discussion of safe equipment.



Cradle for Carrying Gas Cylinders.

Varied Developments in First Quarter on West Coast

WITH the Golden Gate International Exposition at San Francisco now under way, the Pacific Coast refining industry is hopeful that the volume of gasoline, lubricating oil and other service station services and accessories will live up to the predictions which contend that somewhere in the neighborhood of $40,000,000 will be derived from the traffic to the fair.

The curtailment of crude production is still a sore spot. Preliminary efforts as yet have not been productive of the results eventually hoped for. The latest attempt to curtail got under way last November. According to Bureau of Mines figures, the average daily production for the month previous was 659,000 barrels daily. November brought the figure up to 663,000 barrels a day. Disappointment came when the December figure was found to be 646,000 barrels daily, or 46,000 barrels over the 600,000 set as the goal. The federal forecast of demand for December was given as 589,700 barrels.

REFINERY RUNS

With 68 refineries operating, the Pacific Coast's daily capacity amounts to 832,000 barrels. Actual crude run to stills is considerably below this figure as seen by the high of 552,000 barrels and the low of 488,000 barrels daily reached last year. In spite of efforts to bring about voluntary curtailment it is probable that crude runs to stills during the early part of this year will compare closely with last year's figures.

For the past 12 months the monthly production of straight-run gasoline has fallen between 3,235,000 and 3,785,000 barrels, while the volume of cracked gasoline produced has fluctuated between 1,635,000 and 2,250,000 barrels monthly. A good estimate of percent straight-run versus cracked gasoline for the past year would be close to 64 percent for straight-run and 36 percent for cracked. Many observers feel that California should and will crack deeper if economic conditions will ever permit, but that such a step is fruitless until crude production is brought more into line.

A headache to virtually all western refiners is the rate at which huge stocks of fuel oil residuums have been accumulating. One estimate has it that the Pacific Coast is now stocking 66 percent of the available fuel oil in the United States. Stocks of this material have varied between 56,850,000 barrels in January, 1938, to 70,755,000 barrels in December. Added to this would be the 30,000,000 barrels of crude now on hand. So critical has the situation become with some refiners that they have been forced to install heaters in tanks used for other stocks to permit the storage of fuel oil residuum during the winter months. Another concern is reported to have stored over 15,000,000 barrels of residuum.

CONSTRUCTION AND MODERNIZATION

Acid economy, better control of octane value and the minimizing of polymerization effects are said to be prominent among the reasons favoring the increased use of the cold acid treatment of distillates, followed by centrifuging. In this direction Richfield Oil Company has started the year with the announcement of the expenditure of $500,000 for the addition of a Stratcold cold-acid treating plant to its Watson refinery near the Long Beach field. The plant is reported to be of the three-stage type and to have a daily capacity of 10,000 barrels. An elaborate and ultra-modern layout is planned.

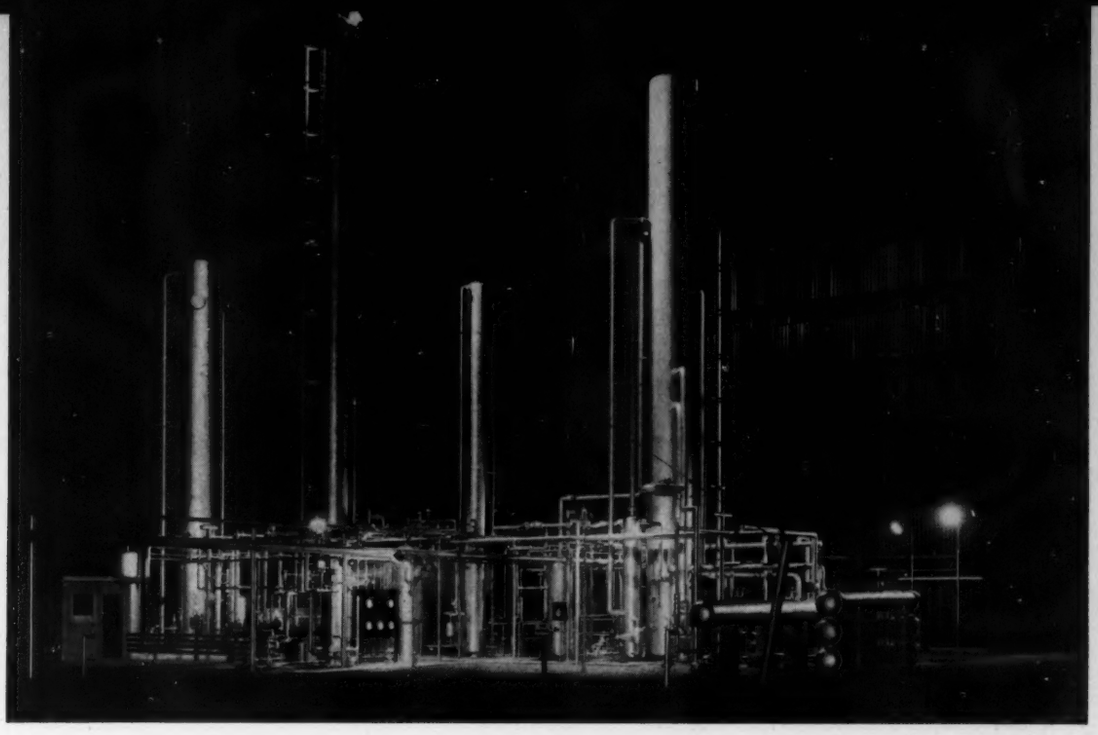
Essentially the Stratcold system (see Composite Catalog of Oil Refinery Equipment, 1938 Ed., page 372) consists of the countercurrent flow of raw distillate against acid through the required number of stages to effect treatment to any desired point. From untreated distillate storage the stock is charged through a settling tank where any free water is removed. From the settling tank the distillate passes through a heat exchanger to a chilling unit refrigerated with ammonia. From the chilling unit the distillate comes into contact with the acid and the acid-distillate mixture enters the first refrigerating contactor. Leaving the contactor, the mixture passes through a centrifuge where the partially treated distillate and sludge are separated. This represents the first stage. The same cycle can be repeated for the desired number of stages.

After the last stage the treated distillate passes through a water wash, a soda contactor and settling tank and finally to finished distillate storage. The first-stage treatment results in the development of most of the sludge. Succeeding stages result in the separation of a progressively treated distillate with less sludge and more residual acid. Partly spent acid is used in the first and succeeding stages with fresh acid applied at the last stage.

In the San Joaquin Valley it is reported that the old Lakeview refinery near Bakersfield has been purchased and will soon be reconditioned and put into operation. If the purchaser's plans materialize the

Selected California Refining Statistics, 1937-1938
(United States Bureau of Mines)

	1938, Barrels	1937, Barrels
Crude oil produced	249,749,000	238,521,000
Crude run to stills	195,069,000	203,145,000
Straight-run produced	43,322,000	47,117,000
Cracked gasoline produced	22,924,000	21,025,000
Kerosene	4,914,000	5,016,000
Lubricating oils	2,609,000	2,568,000



Night view of Rancho Gasoline Corporation's new high-pressure absorption plant at Grapevine, California.

topping and treating equipment will be renovated and additional storage facilities added. The plant has a capacity of 2500 barrels daily.

Shell Oil Company recently completed installation of a complete tank vapor control system at its Dominguez refinery, near Long Beach. The vapor intake and output from eight 80,000 barrel tanks is handled by a steel balloon with a capacity of 350,000 cubic feet of vapor at a pressure of 1-5/8 inches of water. The balloon is 200 feet in diameter.

Ten-inch vapor lines from each tank tie into an 18-inch vapor-collecting line connected with the balloon. As the storage tanks breathe the input and output of vapor from the balloon is carefully balanced. If an excess of vapor over and above the capacity of the balloon develops, the additional amount is picked up by a compressor and liquefied. If a deficiency of vapor occurs within the balloon a dry gas line feeds the amount required through a regulator.

ASPHALT

At its Wilmington refinery Union Oil Company has erected a new plant for air-blowing asphalt. The rest of the equipment has undergone repairs together with the expansion of facilities for the steam refining of asphalt.

In this connection it is interesting to note several points made by R. H. Pierson, of Gilmore Oil Company regarding the applications of asphalt on the Pacific Coast. Citing the paving and roofing industries as the chief users of asphalts, Pierson states that the waterproofing of adobe bricks is an effective use for certain types of asphalt emulsions. In addition to road work, the application of asphalt to airport runways is gaining steadily. It was pointed out that cooling tower basins can be constructed of asphalt, and that concrete basins can be repaired without draining the water by using asphalt patching mixtures which set under water.

RESEARCH AND DEVELOPMENT

The paper on the Houdry catalytic cracking process read before the Chicago A.P.I. meeting has aroused its share of interest on the Pacific Coast. Opinions are divided but it is patent that the various research departments will give the matter a close scrutiny. One argument advanced against catalytic cracking on the Pacific Coast is that of the high natural octane value of western distillates. Others feel that the octane question is secondary to that of the overall economics of the catalytic cracking as compared to crude production. In many quarters the contention is that as long as the overproduction of crude continues there is little incentive to crack deeper. On the other hand if supply and demand can be balanced the picture could change overnight. It has already been rumored that certain types of California crudes work remarkably well in the catalytic system described by Houdry and that work is being done in this direction now in anticipation of future developments. More recently, Standard Oil Company of California has taken out a license to crack catalytically under the Houdry patents.

Standard Oil Company of California has announced the construction of a $300,000 research laboratory adjacent to the refinery at Richmond, a few miles northeast of San Francisco. The structure is to house 12 large air-conditioned laboratories.

NATURAL GASOLINE PRODUCTION

Preliminary totals for 1938 indicate that the Pacific Coast produced 663,992,000 gallons of natural gasoline, or 6 percent over the 623,894,000 gallons produced in 1937. This is the largest volume of natural produced since 1931. If the oil curtailment program is successful, the production of natural gasoline during 1939 might drop. However unforeseen circumstances can alter the picture. For instance, while the present efforts to curtail are based on no large well producing over 300 barrels a day there is no way of offsetting an increase in gas volumes in any district where the total number of wells increase due to drilling developments. The effect of curtailment on oil-to-gas ratios must also be observed carefully before reliable assumptions can be made.

PLANT DESIGN AND OPERATION

Among the interesting developments in plant design is that of the General Petroleum Corporation's gasoline plant in the Wilmington field where sea water is used for cooling. The plant operates without cooling towers. According to M. W. Kibre, the use

Natural Gasoline Produced in 1937 and 1938, by Areas
(United States Bureau of Mines)

	1938, Gallons	1937, Gallons
Appalachian	67,625,000	72,056,000
Illinois, Michigan and Kentucky	12,812,000	12,319,000
Oklahoma	468,460,000	492,290,000
Kansas	54,133,000	57,026,000
Texas	655,835,000	615,281,000
Louisiana	86,693,000	106,415,000
Arkansas	24,235,000	11,285,000
Rocky Mountain	79,529,000	74,868,000
California	663,992,000	623,894,000

of sea water was not only influenced by the savings realizable, but by adverse humidity conditions in and around the Wilmington area.

In laying out the plant and evaluating sea-water cooling, it was determined that if cooling towers were used the system would have to remove 58,000,000 B.t.u. per hour when the plant handled 40,000,000 cubic feet of gas. This would mean a circulation rate of 5000 gallons a minute. Water for this type of cooling would have cost $6,200 yearly. It is reported that the use of sea water has reduced the water cost to a much lower figure and that efficient cooling is obtained because the temperature of the sea water seldom exceeds 70° F., even in summer. The lowest temperature observed has been 57° F.

Sea water is taken from one of the inner channels and pumped to the plant through 2700 feet of 18-inch pipe. The effluent line is 24-inch vitrified pipe. A small amount of well water is used for cooling engine jackets and contains a corrosion-resistant treatment of 240 parts per million of sodium dichromate with enough soda ash (sodium carbonate) to keep the pH at 8.

In using sea water in the coolers, which are made of regular steel pipe, zinc plugs are placed at various points to prevent corrosion. In addition to the zinc plugs the cooler channels are treated with three coats of paint. The first coat is a chromated bakelite type of iron oxide primer. The second coat is a ground coat with a corrosion inhibiting agent; while the third is an anti-fouling mixture of the iron oxide type containing mercuric or cuprous oxide.

Union Oil Company's new single-unit gasoline plant in the Rio Bravo field is at present treating close to 5,000,000 cubic feet of wet gas to produce approximately 3000 gallons of gasoline daily. Shipment is by truck to the company's Maltha refinery near Bakersfield. The plant site covers three acres, and while the present unit occupies but a portion of this, allowances have been made for a potential future expansion to three times the present size. Direct-fired heaters are used instead of steam and the low-pressure gases are compressed to the treating pressure (500 pounds) by a late design angle-type compressor.

Inaugurating a repressuring (or pressure-maintenance) program in the North Belridge field, Belridge Oil Company has recently put into operation a compressor plant which has been pumping close to 10,000,000 cubic feet a day of dry gas into the Temblor formation through four input wells along the edge of the structure. Injection pressure is near 1800 pounds.

Six 300-horsepower angle-type compressors make up the injection plant. Two of the units handle field gas, while the other four take dry gas from the absorbers at 450 pounds and compress it to 1800 pounds, the injection pressure. No cooling is done between stages, as the discharge of one compressor to the next is carried through piping. Power cylinders have a 12-inch by 14-inch bore and stroke; the compression end has a 14-inch stroke; pressure lubrication is supplied to all bearings; and the main bearings are built with removable shells as the lower portion, with babbitt-lined caps for the upper part.

While not the general rule, corrosion of gasoline plant equipment occasionally brings to the attention of the operator the fact that all of the elements are present to contribute to the cost of damage due to corrosion if proper precautions are not taken. Tube bundles, reboilers, absorbers and debutanizers can all be damaged if care is not exercised in the selection of the materials of construction.

J. A. Jamison has commented on a few points which are of practical value. Admiralty metal is suggested as being the most desirable for contact with water in tubular units, particularly with fresh water. Admiralty or carbon steel tubes work well in liquid-to-liquid contacts. If steam is the heating medium in reboilers Admiralty metal again offers good resistance from two to four years. If hot oil is used as the heating medium carbon steel is given as the better. But if it fails an alloy metal containing 4-6 percent chromium and 0.5 percent molybdenum may be necessary.

LIQUEFIED PETROLEUM GAS PRODUCTION

The production of liquefied petroleum gas on the Pacific Coast during 1938 reached a total of 46,000,000 gallons, the largest volume on record. This total is derived from several sources. The major portion, which fluctuated between 3,208,000 and 4,625,000 gallons monthly last year, is manufactured at gasoline plants. Volumes ranging from 600,000 to 1,400,000 gallons monthly are obtained from natural gasoline rectifying operations at refineries, while another portion of the total varying from 500,000 to 1,130,000 gallons monthly is made from cracked gases at refineries. Throughout the past year stocks at the beginning of each month have varied between 1,470,000 to 1,730,000 gallons.

The steady expansion in the use of this commodity is illustrated by the trends in bulk consumption. Butane-operated trucks are to be used in the construction work on the new Shasta Dam. A fleet of 18 trucks is being constructed and powered by 150-horsepower motors. With three times the capacity of the average dump truck, the new units will handle 25 cubic yards at a time. It is also understood that all heating and cooking at the construction camp will be done with liquefied petroleum gas.

At San Pedro, a short time back, the Southern Counties Gas Company tested its $115,000 butane stand-by plant. The installation is fully equipped for automatic performance in the event of emergencies.

The city of Ukiah has changed from the use of manufactured gas to a butane-air mixture.